

YATSIMIRSKII, K. B.

PA 18T91

USSR/Chemistry - Entropy  
Chemistry - Ions

May 1947

"The Standard Entropies of Ions in the Crystalline State," K. B. Yatsimirskii, Chemical-Technological Institute, Ivanovo, 2 pp

"Zhur Fiz Khim" Vol XXI, No 5

Lists the values as discovered by E. N. Gapon and the different values derived by later experimentation. Published 17 Dec 1946.

18T91

YATSIMIRSKIY, K. B.

USSR/Chemistry - Ions  
Chemistry - Cations

Dec 1947

60710 "Thermochemical Radii of Ions in Solution," K. B. Yatimirskiy, 4 pp

60710 "Dokl Akad Nauk SSSR, Nova Ser" Vol LVIII, No 7

Uses method of calculating radii of ions from thermochemical data to calculate this data for several ion solutions. Method consists of finding magnitude of energy of a lattice from thermochemical and spectroscopic data, according to the equation

$$U = -\Delta H_K - \Delta H_X - \Delta H_{KX},$$

where U is the energy of the lattice,  
 $-\Delta H_K, -\Delta H_X$  are the lattice energy of the ions,  
 $-\Delta H_{KX}$  is the energy of the lattice.

60710

USSR/Chemistry - Ions (Contd)

Dec 1947

and  $-\Delta H_{KX}$  are the heat of formation of a gaseous cation, a gaseous anion, and hard salt. Submitted by Academician I. I. Chernyayev, 18 Jun 1947.

60710

The hexachlorostannate series, K. B. Yatskivskii (N. S. Kurakov Inst. Gen. Inorg. Chem. Acad. Sci. U.S.S.R., Moscow). *Invent. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk* 1948, 263-8; cf. *Ibid.* 1946, 461.—The heat of the reaction  $\text{SnCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SnCl}_6^{--}$ , in the gaseous state, is taken = 17.3 kcal./mole, and the radius of the  $\text{SnCl}_6^{--}$  anion = 2.98 Å. (from the  $\text{K}_2\text{SnCl}_6$  lattice). Then by Kapustinakhi's equation for the lattice energy (C.A. 34, 6705) the heat of formation Q of the complex salt from the simple salt and the addend =  $[287.3 + 2(n+m)Z_1/(r_1+2.98)] [1 - [0.345/(r_1+2.98)]] - [287.3Z_2(Z_2+1)/(r_2+1.81)] [1 - [0.345/(r_2+1.81)]] - 17.3$ , where  $r_1$  = radius of the cation, 1.81 = radius of  $\text{Cl}^-$ ,  $Z_1$  = charge of the cation, n = no. of cations, m = no. of  $\text{SnCl}_6^{--}$  anions in the mol. Numerical solution of this equation gives the conditions of stability of hexachlorostannates, namely, for salts of the type  $M^{\text{II}}(\text{SnCl}_6)_Q$ ,  $Q > 0$  if  $r_2 > 0.4$  Å., for salts of the type  $M^{\text{III}}(\text{SnCl}_6)_Q$ ,  $Q > 0$  if  $r_2 > 1.5$  Å., and for salts of the type  $M^{\text{IV}}(\text{SnCl}_6)_Q$ ,  $Q > 0$  if  $r_2 > 3.7$  Å. It accounts satisfactorily for the fact that, although chlorostannates of  $[\text{M}^{\text{II}}(\text{H}_2\text{O})]^{++}$  aquo cations are stable, those of the anhyd. simple cations  $M^{\text{II}}$  are not, as the latter do not attain the crit. size of 1.5 Å. There are no chlorostannates of  $\text{Ba}^{++}$  or  $\text{Pb}^{++}$ , as these cations form no stable aquo ions. It further becomes evident why chlorostannates of big cations such as  $[\text{M}(\text{CON}_2\text{H}_2)_6]^{++}$  are stable. The following chlorostannates were prepd.: By mixing the stoichiometric amts. of  $\text{FeCl}_3$ ,  $\text{CO}(\text{NH}_2)_2$ , and  $\text{SnCl}_4$  and evap. on a water bath to becoming crystals, one obtains  $[\text{Fe}(\text{CON}_2\text{H}_2)_6](\text{Cl})(\text{SnCl}_6)$ . readily sol. in  $\text{H}_2\text{O}$ , stable in air, losing  $\text{H}_2\text{O}$  at  $70-80^\circ$ ; with excess  $\text{SnCl}_4$ , one gets the yellowish  $[\text{Fe}(\text{CON}_2\text{H}_2)_6](\text{SnCl}_6)_2 \cdot 15\text{H}_2\text{O}$ . On mixing concd. solns. of  $[\text{Cr}(\text{CON}_2\text{H}_2)_6]\text{Cl}_3$  and  $\text{SnCl}_4$ , one obtains a ppt. of light-green crystals  $[\text{Cr}(\text{CON}_2\text{H}_2)_6](\text{Cl})(\text{SnCl}_6)$ , stable in air, losing  $\text{H}_2\text{O}$  at  $90-100^\circ$ . When the calcd. amts. of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and of  $\text{CO}(\text{NH}_2)_2$  are dissolved in a 60% aq. soln. of  $\text{SnCl}_4$ , and the soln. is heated 10-20 min. on a water bath and left in a desiccator over  $\text{H}_2\text{SO}_4$  for 5-6 days, the salt  $[\text{Ca}(\text{CON}_2\text{H}_2)_6](\text{SnCl}_6)$  is pptd.  $[\text{Mg}(\text{CON}_2\text{H}_2)_6]$ - $\text{SnCl}_6$  is obtained in an analogous way. N. Thon

ASS-SLA METALLURGICAL LITERATURE CLASSIFICATION

RECORD SYSTEM

RECORD NUMBER

RECORD DATE

RECORD TIME

YATSIMIRSKIY, K.B.

Yatsemir-skiy, K.B. and Zaslavskiy, I.I. "Classification of diagrams in volumetric analysis of liquid double systems," (reference), Soobshch. o nauch. rabotakh chlenov Vsesoyuz. khim. o-va im. Mendleyeva, 1948, Issue 2, p. 23

SO: U-2888, Letopis Zhurnal'nykh Statey, No. 1, 1949

YATSIMIRSKIY, K. B.

8/49T13

USSR/Chemistry - Heat of Hydration, Of Ions Jul/Aug 48  
Chemistry - Thermochemistry

"Thermochemical Radii and Heats of Hydration of Ions,"  
K. B. Yatsimirskiy, Inst Gen and Inorg Chem Iment N. S.  
Kurnakov, Acad Sci USSR, 7 1/2 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 4

Calculates thermochemical radii and heats of formation  
in the gaseous state of the ions:  $\text{JO}_3$ ,  $\text{BrO}_3$ ,  $\text{CNO}'$ ;  
 $\text{C}_6\text{H}_5(\text{NO}_2)_3\text{O}'$  and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]$ .  
Calculates heats of hydration of the ions:  
 $\text{ClO}_4$ ,  $\text{C}_6\text{H}_5(\text{NO}_2)_3\text{O}'$ ,  $\text{ClO}_3$ ,  $\text{BrO}_3$ ,  $\text{NO}_3$ ,  $\text{HCO}_3$ ,  $\text{CNO}'$ ,  
 $\text{H}_2\text{COO}'$ ,  $\text{KCO}_3$ ,  $\text{CNS}'$ ,  $\text{CN}'$ ,  $[\text{N}(\text{CH}_3)_4]$  and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]$ .  
Shows relation between heat of hydration and magnitude  
8/49T13

USSR/Chemistry - Heat of Hydration, Of Ions Jul/Aug 48  
(Contd)

of thermochemical radius. This relation for anions of  
the type  $\text{RO}_n$  is somewhat different from that for other  
anions. Shows applicability of Kapustinskii's  
equation for calculating the entropies of  $\text{RO}_n$  type  
ions in aqueous solution. Presents heat  
of solution of salts as a function of the ion radii  
which form the particular salt. Establishes general  
relationship between alteration of heat of solution and  
the magnitude of the ion radii. Submitted 11 Jun 1947.

8/49T13

YATSMIRSKIY, K. B.

PA 27/49T32

USSR/Chemistry - Lanthanum Compounds Sep/Oct 48  
Chemistry - Ionization, Potential of

"Calculation of the Potentials of Ionization for  
Some Lanthanides by Means of Kapustinskiy's  
Equation," K. B. Yatsmirskiy, Inst Gen and Inorg  
Chem imeni N. S. Kurnakov, Acad Sci USSR, Ivanovo  
Chem Eng Inst, 2 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 5

Found a regular increase in the ionization potential  
of the lanthanide series, Ce-37.1 ev, Pr-37.7 ev,  
Nd-38.2 ev, Sm-38.2 ev, and Er-40.0 ev. Submitted  
5 Apr 48.

27/49T32

YATSIMIRSKIY, K. B.

PA 33/49T20

USSR/Chemistry - Synthesis  
Chemistry - Energy, Lattice, of Metal Salts  
Nov/Dec 48

"The Lattice Energy of Metal Salts of Secondary  
Groups in a Periodic System," K. B. Yatsimirskiy,  
Inst Gen and Inorg Chem imeni N. S. Kurnakov,  
Acad Sci USSR, 11 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 6

Studies condensation of 2-formoxybutadiene, 2-  
methoxybutadiene, and chloroprene with divinylke-  
tones (5-methyl-1,4-hexadiene-3-onium and 5-  
methyl-1,4-octadiene-3-onium). Shows that re-  
action takes place easily according to General

33/49T20

USSR/Chemistry - Synthesis (Contd) Nov/Dec 48

diagram of diene synthesis with formation of  
corresponding pair-substituted derivatives of  
cyclohexenylketones. Submitted 10 Nov 47.

33/49T20



YATSIMIRSKIY, K. B.

PA 67/49T40

USSR/Chemistry - Salts, Ammine  
Cobalt

Dec 48

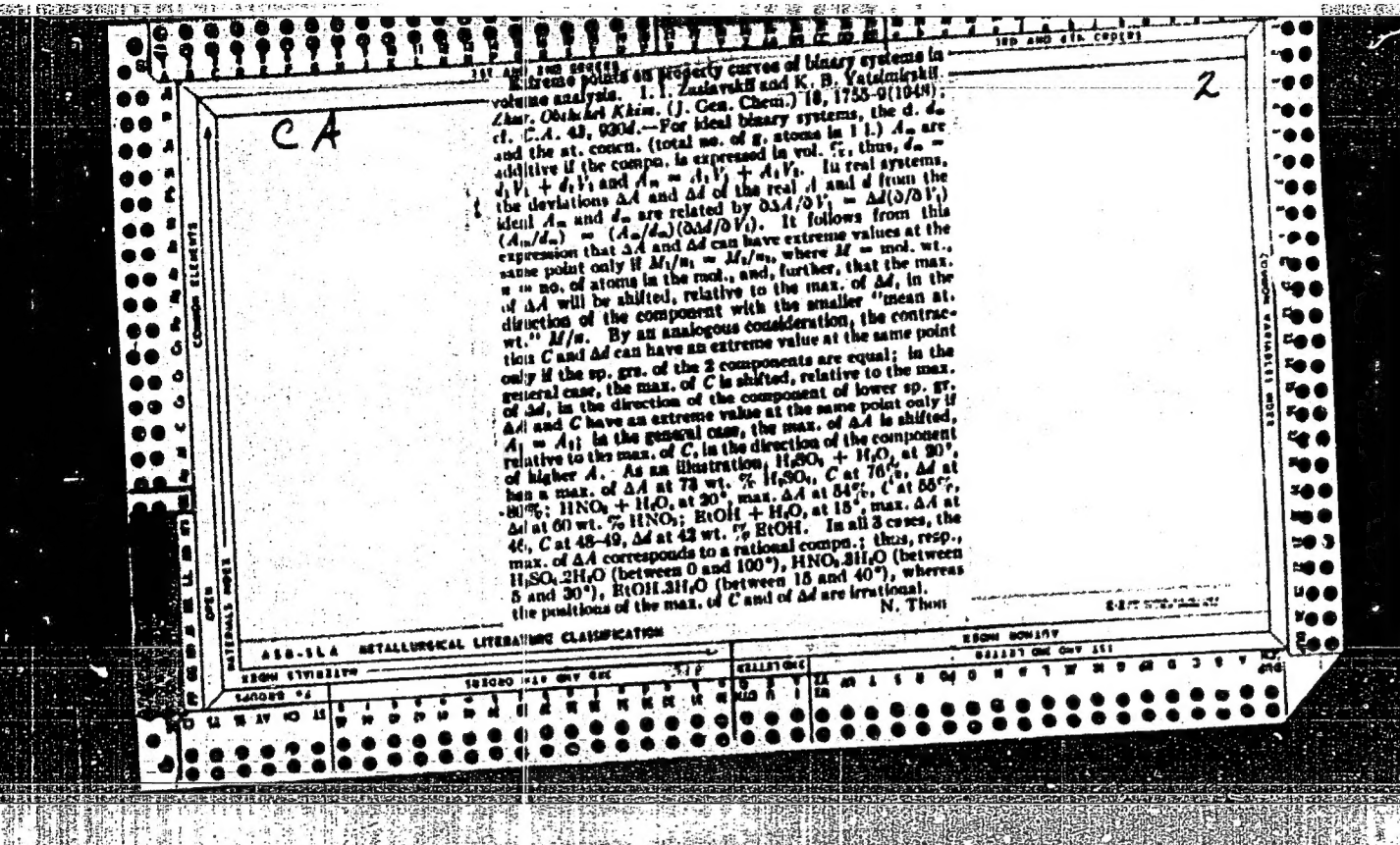
"Thermochemistry of Cobalt Acidopentamine Salts,"  
K. B. Yatsimirskiy, L. L. Pankova, Chair of  
Inorg Chem, Ivanovo Chemicotechnol Inst., 7 $\frac{1}{2}$  pp

"Zhur Obsluch Khim" Vol XVIII, No 12

Determined heats of formation and heats of  
solution for a large number of salts such as  
(Co(NH<sub>3</sub>)<sub>5</sub>Cl)Br<sub>2</sub>, (Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>)I, etc. Made a  
study of the thermochemistry of their ions.

67/49T40





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B

ENTROPIES OF IONS IN CRYSTALS AND SOLUBILITY OF SALTS.  
(In Russian.) A. F. Kapustinikil and K. B. Yatsi-  
mirskii, *Zhurnal Fizicheskoi Khimii* (Journal of  
Physical Chemistry), v. 22, Oct. 1948, p. 1271-1279.  
Presents results of experimental and theoretical  
study. Data are tabulated and charted. 15 ref.

ASACSLA METALLURGICAL LITERATURE CLASSIFICATION

IATSIMIRSKII, K. B.

I. I. Zaslovskii and K. B. Iatsimirskii, Unusual points on the curves of properties of binary systems during volumetric analysis. p. 1755

Mathematical analysis has established the following for 2-compound systems by chemical reaction: The maximum deviation of atomic concentration from the average of calculated value ( $\Delta A$ ) is shifted in regards to the maximum deviation of specific gravity from the average calculated value ( $\Delta d$ ) toward the component with the smaller average atomic weight. The maximum  $\Delta A$  is shifted in regard to the compression maximum  $C$  toward the component with the largest atomic concentration. The maximum  $\Delta d$  is shifted in regards to the maximum  $C$  toward the component with the largest specific gravity.

✓ Chair of Inorganic Chemistry of the Ivanov Chemical Technological Institute  
July 17, 1947

SO: Journal of General Chemistry (USSR) 28, (80) No. 10 (1948):

YAKIMIRSKIY, K. B.,

K. B. Yakimirskii and L. L. Pankova, Thermo-chemistry of acido-pentaammine salts of cobalt. p. 2051.

The heat of reaction is determined with a 0.26 in solution of  $\text{Na}_2\text{S}$  and from this is calculated the heat of formation of 15 compounds and the heat of solution of 13 compounds. The heat of formation is calculated for a series of complex acido-penta-ammine cobalt-ions in a water solution. From this is calculated the heat of formation of certain salts.

Chair of Inorganic Chemistry of the  
Ivanov Chemico-Technological  
Institute  
June 28, 1947

SO: Journal of General Chemistry (USSR) 28, (80) No. 12, (1948)

YATSIMIRSKIY, K.B.

29573

Ie istorii analitichyeskoy khimii v rossii. Uspyekhi Khimii,  
1949, vyp.5, s.623-28. Bibliogr: s.628

4. Gyeologo-Gyeorafichyeskiye Nauki  
(Palyeontologiya - Sm. XV, 5 B)

a. Gyeologo-Gyeografichyeskiye Nauki b Tsyelom. Gyeologiya. Pyetrografiya.  
Minyeralogiya. Kristallografiya.

SO: LETOPIS' NO. 40

1ST AND 2ND ORDERS										3RD AND 4TH ORDERS									
PROCESSES AND PROPERTIES INDEX																			
<p>3014 The Energetics of the Lanthanide Ions. K. B. Yatsimirskii. Invest. Akad. Nauk S.S.S.R., Otd. Khim. Nauk, No. 6, 648-511(1949)(in Russian).</p> <p>Thermochemical characteristics of rare earths, such as ionization potentials, and hydration and formation heats, of their trivalent ions, were determined by using the equation of Kapustin'skiĭ (Zhur. Obshchei Khim. 13, 497(1943)) and the known thermochemical data. Thus, the formation heats <math>-H_2</math> of the gaseous ions <math>La^{3+}</math>, <math>Ce^{3+}</math>, <math>Pr^{3+}</math>, <math>Nd^{3+}</math>, <math>Gd^{3+}</math>, <math>Dy^{3+}</math>, <math>Ho^{3+}</math>, <math>Er^{3+}</math>, <math>Tm^{3+}</math>, and <math>Lu^{3+}</math> were found from <math>-H_2 = 3H_{Cl} - U_{Cl_2} - H_{Cl_2}</math>, where <math>H_{Cl_2}</math> and <math>-H_{Cl_2}</math> are formation heats of the gaseous <math>Cl_2</math> and the solid salt, respectively, and <math>U_{Cl_2}</math> is the energy of the latter's lattice, calculated from Kapustin'skiĭ's equation. Since the formation heat of a gaseous ion is the sum of the metal's sublimation and ionization heats, and since the ionization heat is approximately equal to the ionization potential <math>I</math>, the latter can be calculated, by using the value 90 kcal for the sublimation heat of the lanthanides. The values found satisfy the equation <math>I = 43.18 \log Z - 38.9</math>, from which the ionization potential of the element 61, <math>Eu^{3+}</math>, <math>Tb^{3+}</math>, and <math>Yb^{3+}</math>, can be calculated. Further, the hydration heats <math>L_H = -H_{aq} + H_2 - 3 \times 101</math>, where 101 kcal is the heat of formation of a H ion in water solution, and the difference <math>H_{aq} - 303</math> is the heat of formation of a trivalent lanthanide ion in water solution. The values thus calculated satisfy the equation <math>L_H = 382 + 319/r</math>, where <math>r</math> is the ion radius. By using the material obtained in the present work, an estimation can be made of the heats of formation of various compounds, such as chlorides, hydroxides, oxides, nitrates, sulfates, etc., of the lanthanides.</p>																			
<p>ASB-5LA METALLURGICAL LITERATURE CLASSIFICATION</p>																			
FROM SYMBOL										FROM NUMBER									
<p>1ST ORDER 2ND ORDER 3RD ORDER 4TH ORDER 5TH ORDER 6TH ORDER 7TH ORDER 8TH ORDER 9TH ORDER 10TH ORDER</p>										<p>1ST ORDER 2ND ORDER 3RD ORDER 4TH ORDER 5TH ORDER 6TH ORDER 7TH ORDER 8TH ORDER 9TH ORDER 10TH ORDER</p>									

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Diagrams of the type ionic radii-property. K. B. Yatsinskii (Ivanovo Chem.-Technol. Inst., Ivanovo, U.S.S.R.). *Izvest. Sektora Fiz.-Khim. Anal. Inst. Obshch. i Neorg. Khim., Akad. Nauk S.S.S.R.* No. 19, 203-10 (1949). —For this type of diagram where the properties are lattice energy, heat of soln., and soly. cf. *C.A.* 42, 4890c, 6804c, and 43, 1341f. Analogous diagrams were constructed for ionic radii vs.  $\mu$ , ps. The diagram ionic radii-crystal structure differed from the preceding ones. When values of  $r_+$  were plotted as abscissa and  $r_-$  as ordinate, where  $c$  and  $a$  designate cation and anion, resp., and when line  $AB$  was drawn for  $r_+/r_- > 0.87$  and line  $CD$  for  $r_+/r_- = 0.41$ , it could be expected, according to Magnus and to Goldschmidt, that to the right of  $AB$  the crystal structure would be that of  $\text{CaCl}_2$ , yet out of 10 salts 3 crystal, as expected, 9 were of the  $\text{NaCl}$  type, and 7 had both structures. Similarly, between  $AB$  and  $CD$  the  $\text{NaCl}$  type of structure was expected, yet  $\text{NH}_4\text{I}$  having both types of structure was located there. The diagram showed that the  $\text{CaCl}_2$  structure appeared where  $r_+ > 1.6 \text{ \AA.}$  and  $r_- > 1.9 \text{ \AA.}$  Both  $\text{CaCl}_2$  and  $\text{NaCl}$  types occurred where  $r_+ > 1.35 \text{ \AA.}$  and  $r_- > 1.7 \text{ \AA.}$  Thus, the type of crystal structure depended on the absolute value of  $r$ . M. Hensch



CA

Thermochemistry of complex cobaltic salts with neutral  
additives. K. D. Yablinskii and I. L. Pankova (Ivan-  
ovo Inst. Chem. Technol.). *J. Gen. Chem. U.S.S.R.*  
10, 800-75(1919) (English translation).—See C.A. 43,  
7915g. R. J. C.

C4

2

Thermochemical reactions in the Werner-Mischel  
series for complex cobaltic compounds. K. B. Yashinski-  
ski and L. L. Pashova (Institute of Chem. Technol.),  
J. Gen. Chem. U.S.S.R. 19, 677-68 (1948) (English trans-  
lation).—(see C.A. 43, 7836c. E. J. C.

CH

2

Thermochemical radii and energies of tetrahedral and triangular ions. A. P. Kapustin and K. B. Yatsimirskii (Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshch. Khim.* (J. Gen. Chem.) 19, 2191-2200 (1949). (1) Thermochem. radii  $r$  calcd. for a given anion by K.'s equation (C.A. 24, 3709) from the lattice energy  $U$ , show very slight variations, of the order of 3%, depending on the nature of the cation of the salt, in the sense that  $r$  of the nonspherical anion increases when it is assoc. with a larger cation;

e.g.,  $\text{NO}_3^-$ ,  $r$  varies from 1.86 in  $\text{CaNO}_3$  to 1.94 A. in  $[\text{Co}(\text{NH}_3)_6][\text{NO}_3]_2$ ;  $\text{ClO}_4^-$  from 1.98 in  $\text{RbClO}_4$  to 2.06 A. in  $[\text{Ni}(\text{H}_2\text{O})_6][\text{ClO}_4]_2$ ;  $\text{HCO}_3^-$  from 1.56 in  $[\text{Zn}(\text{NH}_3)_6](\text{HCO}_3)_2$  to 1.60 in  $[\text{Cu}(\text{NH}_3)_4](\text{HCO}_3)_2$ ;  $\text{SO}_4^{--}$  from 2.33 in  $\text{CaSO}_4$  to 2.33 in  $[\text{Co}(\text{NH}_3)_6][\text{SO}_4]$ ;  $\text{CrO}_4^{--}$  from 2.37 in  $[\text{Co}(\text{NH}_3)_6]\text{BrCrO}_4$  to 2.43 in  $[\text{Co}(\text{NH}_3)_6]\text{NO}_3\text{CrO}_4$ ;  $\text{O}_4^{--}$ , 1.79 in  $\text{BaO}_4$ , 1.80 in  $\text{CaO}_4$  and  $\text{BrO}_4$ . A smaller cation penetrates more deeply into recesses of the anion and thus brings about a decrease of its  $r$ . (2) In heats of hydration  $Q$  of anhyd. salts, calcd. by  $Q = U_0 - U + W$ , where  $U_0$  = lattice energy of the hydrated salt, the heat of formation  $W$  of the gaseous aquo ion from the gaseous central ion and gaseous  $\text{H}_2\text{O}$  remains const. in the case of salts of spherical anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) but anomalies appear with nonspherical anions; thus, instead of increasing with the size of the anion,  $Q$  is greater for chlorides than for nitrates, and the same reversal

is found between bromides and chlorates. This reversal is due to a decrease of the "penetration effect," present in the case of polyst. anions, as a result of the hydration of the cation. Illustrative data of  $Q$ , in kcal./mole, are:  $[\text{Li}(\text{H}_2\text{O})_6]\text{Cl}$  42.3,  $[\text{Li}(\text{H}_2\text{O})_6]\text{NO}_3$  40.0,  $[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}$  36.9,  $[\text{Mg}(\text{H}_2\text{O})_6]\text{NO}_3$  28.8,  $[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}$  36.3,  $[\text{Ca}(\text{H}_2\text{O})_6]\text{Cl}$  11.8,  $[\text{Ca}(\text{H}_2\text{O})_6]\text{NO}_3$  14.0,  $[\text{Ca}(\text{H}_2\text{O})_6]\text{Cl}$  89.4,  $[\text{Ca}(\text{H}_2\text{O})_6]\text{NO}_3$  84.4,  $[\text{Ba}(\text{H}_2\text{O})_6]\text{Br}$  10.6,  $[\text{Ba}(\text{H}_2\text{O})_6](\text{ClO}_4)$  14.4,  $[\text{Ba}(\text{H}_2\text{O})_6]\text{Cl}$  15.3,  $[\text{Ba}(\text{H}_2\text{O})_6](\text{IO}_4)$  12.7. (3) The value of  $r$  lies somewhere between the min. distance of max. penetration and the radius of the circumscribed sphere. The distance  $d$  between the central atom of the complex anion and the cation is not equal to the sum of the thermochem. radii  $r$  calcd. for an octahedral surrounding, but, for a given lattice type, the ratio of  $d$  and the sum of  $r$  is a const.; thus, for the barite type ( $\text{BaSO}_4$ ,  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ ), that ratio = 1.05, and for the calcite type ( $\text{CaCO}_3$ ,  $\text{MnCO}_3$ ,  $\text{NaNO}_3$ ), 0.90. For a given type of anion, the ratio of  $r$  and the radius of the circumscribed sphere is a const., thus, for triangular ions ( $\text{NO}_3^-$ ,  $\text{CO}_3^{--}$ ) it is = 0.67; for tetrahedral ions ( $\text{ClO}_4^-$ ,  $\text{MnO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{SO}_4^{--}$ ,  $\text{CrO}_4^{--}$ ,  $\text{MoO}_4^{--}$ ) it varies between 0.76 and 0.81, mean 0.79 = 0.03. This relation permits calcu.

over

of  $r$  for anions for which the radius of the circumscribed sphere is known; thus, for  $\text{BO}_3^{--}$ ,  $r$  (calcd.) = 1.91,  $\text{BeF}_4^{--}$  2.45,  $\text{IO}_4^{--}$  2.49,  $\text{SeO}_4^{--}$  2.43,  $\text{TeO}_4^{--}$  2.54,  $\text{PO}_4^{--}$  2.38,  $\text{AsO}_4^{--}$  2.48,  $\text{SbO}_4^{--}$  2.60,  $\text{BiO}_4^{--}$  2.66 Å. (4) In groups of the periodic system, the  $r$  of anions of analogous structure increase regularly with increasing at. no. of the elements. (5) Heats of formation of the gaseous anion are calcd. by  $-\Delta H_A = \Delta H_f - \Delta H_{fA} - U_{CA}$ , where the subscripts  $A$ ,  $C$ , and  $CA$  refer to the gaseous anion, the gaseous cation, and the solid salt, resp., and the  $\Delta H_f$  are calcd. from the ionization potentials and the heats of sublimation of the metals; for  $\text{TeO}_4^{--}$  and  $\text{SbO}_4^{--}$ , the  $\Delta H_A$  were calcd. from the heats of formation of the ions in soln., and their heats of hydration  $Q$ . Values of  $r$ ,  $\Delta H_A$ , and  $Q$ , are:  $\text{NO}_3^-$  1.89, 80.0, 70.7;  $\text{ClO}_3^-$  2.00, 87.5, 64;  $\text{ClO}_2^-$  2.38, 91.5, 80;  $\text{MnO}_4^{--}$  2.40, 174, 49;  $\text{IO}_3^-$  2.48, 98, (40);  $\text{CO}_3^{--}$  1.85, 47, 317;  $\text{CrO}_4^{--}$  2.4, 182, 229;  $\text{SO}_3^{--}$  2.3, 178, 241;  $\text{SeO}_3^{--}$  2.43, 124, 224;  $\text{MoO}_4^{--}$  2.51, 230, 216;  $\text{TeO}_3^{--}$  2.54, 188, (216);  $\text{WO}_4^{--}$  2.57, 266, 201;  $\text{BO}_2^{--}$  1.91, -240, 700;  $\text{PO}_2^{--}$  2.38, 50, 530;  $\text{AsO}_2^{--}$  2.48, -20, 530;  $\text{SbO}_2^{--}$  2.60, -20, (515);  $\text{BiO}_2^{--}$  2.6, (-330), --. (6) The calcd. values of  $-\Delta H_A$  permit a decision between the Kossel scheme representing the structure of the  $\text{BO}_3^{--}$  ion by ionic bonds between a cen-

tral  $\text{B}^{3+}$  ion and 4  $\text{O}^{--}$  ions, and the Lewis scheme involving covalent bonds between  $\text{B}^{3+}$  and 4  $\text{O}^-$ . The energy of the process  $\text{B}^{3+} + 4 \text{O}^{--} = \text{BO}_3^{--}$  is calcd. to be 4000 kcal., that of  $\text{B}^{3+} + 4 \text{O}^- = \text{BO}_3^{--}$  to be 725, as against 7340 and 1000 kcal., resp., from the  $\Delta H_A$  data. Consequently, the Lewis structure is distinctly predominating. The same holds for the anions  $\text{ClO}_3^-$ ,  $\text{PO}_4^{--}$ ,  $\text{SiO}_4^{--}$ ,  $\text{AsO}_4^{--}$ ,  $\text{SbO}_4^{--}$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{--}$ ,  $\text{BO}_3^{--}$ ,  $\text{ClO}_2^-$ , all of which prove to be predominantly built of singly charged  $\text{O}^-$  ions covalently bonded with the central ion. The Kossel structures become somewhat more probable as the degree of oxidation of the central ion decreases, but their share never becomes significant. (7) Exptl. detn. of the heat of soln. of  $\text{NaIO}_3$  in  $\text{H}_2\text{O}$  at 25° gave -8910 cal.; with the

heat of formation of  $\text{NaIO}_3$  in aq. soln. = 95.1 kcal.; this gives for solid  $\text{NaIO}_3$ ,  $\Delta H_{\text{sol}} = -104.0$  kcal.

N. Thon

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CH

Thermochemistry of aqueous salts of manganese. K. B. Valentinov and A. A. Astasheva (Izvestiya Khim.-Tekhnol. Inst., Doklady Akad. Nauk S.S.S.R. 69, 381-3 (1948); *ibid.* 20, 1407 (1947); C.A. 43, 2168d. --- Owing to the difficulty of prep.  $[Mn(H_2O)_6]Cl_2$  with exactly 4  $H_2O$ , the heat of soln. in  $H_2O$ , at 25 = 0.08°, is reported as a means of 11 determ. made on preps. with 4.3, 4.08, 4.08, 3.98, and 3.7  $H_2O$ ; the av. value later pointed to 4  $H_2O$  is 8680 cal., different from the figure of Thomson and of Farver (C.A. 20, 8228°). This gives for the heat of formation  $\Delta H_{f, aq}^\circ = -398.7$  kcal. Further detns. of heats of soln. gave:  $[Mn(H_2O)_6]Br_2$  4020 cal.,  $\Delta H_{f, aq}^\circ = -276.1$  kcal.;  $[Mn(H_2O)_6]I_2$  3480 cal.,  $\Delta H_{f, aq}^\circ = -241.0$  kcal.;  $[Mn(H_2O)_6]Br_2$  at 0° (because of the decomposition above 13°), -408 cal.;  $\Delta H_{f, aq}^\circ = -317.3$  kcal. With the previously detd. heat of soln. of 6  $H_2O$  (gas) to  $Mn^{++}$  (gas), -288 kcal., and  $Mn^{++}$  (gas) + 4  $H_2O$  (gas) =  $[Mn(H_2O)_4]^{++}$  (gas) - 188 kcal., based on the calns. of Hey and Evans (C.A. 22, 8227°), the heat of formation of the gaseous ion  $[Mn(H_2O)_4]^{++}$  is  $\Delta H_{f, gas}^\circ = 177$  kcal. Hence, by the energy difference of the solid salt and the gaseous ions, the lattice energy of solid  $[Mn(H_2O)_6]Cl_2$  is 480.7 kcal., and, by the equation of Kapustinikh (C.A. 23, 5708°), the thermodynam. radius of  $[Mn(H_2O)_6]^{++}$  is 1.63 Å. The calcd.  $\Delta H_{f, aq}^\circ$  values are in very good agreement with the exptl. values, but differ, by 11.4-13.7 kcal., from the figures of Bichowsky and Rossini, which are based on old erroneous data of Leconte (*Ann. chim. phys.* 28, 423 (1843)). N. Thou

LA

2

**Classification of diagrams in volume analysis of liquid binary systems.** K. B. Yatsimirskii and I. I. Zaslavskii (Izv. Akad. Nauk SSSR, Khim. i Mekh. Zhidk. i Gaz. (1960), 10, 201 (1960)). Diagrams of the activity  $A$  as a function of the composition are of 4 types: In ideal systems of noninteracting liquids of unchanging degree of assoc.,  $A$  is a linear function of the compn., and the deviation  $\Delta A$  from additivity is zero throughout. In systems with one assoc. component which, in soln., dissociates into simpler units, the curve of  $\Delta A$  is convex to the axis of compn., and  $\Delta A$  is always neg. In systems where the components form chem. compds.,  $\Delta A$  is concave to the axis of the compn. In systems involving both compd. formation and dissociation of one or both assoc. components, the  $\Delta A$  curve is slightly concave to the axis of abscissas; the abs. values of  $\Delta A$  are relatively low, and the max. of  $\Delta A$  may not correspond to the compn. of the compd. Examples of ideal systems are  $\text{EtOH}-\text{AcOH}$ ,  $\text{C}_6\text{H}_6-\text{CCl}_4$ ,  $\text{C}_6\text{H}_6-\text{PhBr}$ ,  $\text{AcOH}-\text{HCO}_2\text{Et}$ ,  $\text{C}_6\text{H}_6-\text{PhCl}$ ,  $\text{C}_6\text{H}_6-\text{PhMe}$ ,  $\text{CCl}_4-\text{PhMe}$ ,  $\text{CCl}_4-\text{C}_6\text{H}_5\text{Br}$ ,  $\text{C}_6\text{H}_6-\text{C}_6\text{H}_5\text{Br}$ , etc.; for all these systems, plots of  $\Delta A$  and of the sp. gr. against the compn. in mole fractions are linear, although the viscosity isotherms may show a min. or a max. Linear plots of  $\Delta A$  may be found also with systems of assoc. but chemically close substances, as  $\text{MeOH}-\text{PrOH}$  and  $\text{HCO}_2\text{H}-\text{AcOH}$ . Very slight deviations from additivity, with consistently neg.  $\Delta A$ , are exhibited by  $\text{CCl}_4-\text{CS}_2$ ,  $\text{PhMe}-\text{CS}_2$ ,  $\text{CHCl}_3-\text{CS}_2$ ,  $\text{C}_6\text{H}_5\text{Br}-\text{CS}_2$ ,  $\text{C}_6\text{H}_5-\text{CS}_2$ ,  $\text{CCl}_4-\text{CHCl}_3$ ,  $\text{C}_6\text{H}_6-\text{Et}_2\text{O}$ ,  $\text{C}_6\text{H}_6-\text{C}_6\text{H}_5\text{Br}$ , etc.; very small pos.  $\Delta A$  is found in  $\text{C}_6\text{H}_5\text{Br}-\text{CHCl}_3$  and  $\text{CS}_2-\text{PhBr}$ . The 2nd type, with dis-

tinctly neg.  $\Delta A$ , is exemplified by  $\text{C}_6\text{H}_5-\text{AcOH}$ ,  $\text{CCl}_4-\text{Me}_2\text{CO}$ ,  $\text{CS}_2-\text{Me}_2\text{CO}$ ,  $\text{EtBr}-\text{AcOH}$ ,  $\text{PhMe}-\text{AcOH}$ ,  $\text{CCl}_4-\text{PrOH}$ ,  $\text{MeI}-\text{Me}_2\text{CO}$ ,  $\text{CS}_2-\text{PrOH}$ , etc.; viscosity isotherms of some of these systems may have either a min. or a max., and are, consequently, less informative than the  $\Delta A$  plots. In the 3rd type, the  $\Delta A$  curve consists of 2 branches intersecting at the max.; depending on whether, along a branch,  $A$  and  $\Delta A$  are syzygetic, antibatic, or const., the branch is convex to the axis of compn., concave to it, or rectilinear. One single compd. is indicated by a singular point, whereas in the case of presence of several compds., the max. is rounded, as in  $\text{HClO}_4-\text{H}_2\text{O}$ ,  $\text{HNO}_3-\text{H}_2\text{O}$ ,  $\text{HF}-\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_4-\text{H}_2\text{O}$ ,  $\text{N}_2\text{H}_4-\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4-\text{Et}_2\text{O}$ , etc. "Irrational" systems of the 4th type, showing a flat diffuse max., are illustrated by  $\text{PhOH}-\text{PhNH}_2$ ,  $\text{Me}_2\text{CO}-\text{HCO}_2\text{H}$ ,  $\text{C}_6\text{H}_5-\text{N}_2\text{H}_4$ ,  $\text{H}_2\text{O}$ , etc. In the systems  $\text{AcOH}-\text{H}_2\text{O}$ ,  $\text{MeOH}-\text{H}_2\text{O}$ ,  $\text{Me}_2\text{CO}-\text{AcOH}$ ,  $\text{PhOH}-\text{Me}_2\text{CO}$ , the max. corresponds to no stoichiometric ratio of the components and to no definite compd. An S-shaped  $\Delta A$  curve, resulting from the predominance of the dissociation of an assoc. component along part of the curve, and of compd. formation along another part, is exemplified by the systems  $\text{SbCl}_3-\text{C}_6\text{H}_6$ ,  $\text{SbCl}_3-\text{CHPh}_3$ , and  $\text{SbCl}_3-\text{C}_6\text{H}_5$ , where, again, the max. corresponds to no stoichiometric ratio of the components.

N. Thon

CA

2

Classification of complex-forming elements and addends on the basis of energy characteristics. K. H. Vatsilyashvili (Yanov Chem.-Technol. Inst.). Zhuravskii, A. M. (Izv. Akad. Nauk SSSR, Ser. Khim., 1961, 7(1961)). In the general case, the energy of formation  $\Delta H$  of a complex ion from the gaseous central ion and the gaseous addends ("energy of addn.") is composed of electrostatic and covalent terms; specifically, if  $n$  is the no. of donor-acceptor covalent bonds in the complex ion,  $\Delta H = I - nE - nD + U$ , where  $I$  = total ionization potential,  $E$  = electron affinity of the addend,  $D$  = energy of the covalent bond between the central ion and the addend, and  $U$  = resonance energy of the given structure. On that basis, both complex-forming central elements and addends can be classified, roughly, in 4 groups: (1) "electrostatic," characterized by a high elec. charge, small radius  $r$ , high dipole moment, relatively low  $I$ , and high  $E$ ; examples of central atoms are  $Al^{3+}$ ,  $Ti^{4+}$ ,  $Zr^{4+}$ ,  $Hf^{4+}$ , and of addends,  $F^-$ ,  $H_2O$ ,  $ROH$ ,  $CO_3^{2-}$ ,  $SO_4^{2-}$ ; (2) "covalent," characterized by high  $I$ , low  $E$ , low electrostatic characteristics; examples of central atoms are  $Au^+$ ,  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Bi^{3+}$ ,  $Tl^+$ , addends  $S_2O_8^{2-}$ ,  $I^-$ ,  $CNS^-$ ,  $Br^-$ ,  $CSN_2$ ,  $Li^+$ ; (3) "universal," characterized by high  $I$ , low  $E$ , high elec. charge and small  $r$ ; examples are  $Co^{3+}$ ,  $Pt^{4+}$ ,  $Rh^{3+}$ ,  $Ir^{3+}$ ,  $Cr^{6+}$ ,  $Cu^{2+}$ , and the addends  $CO_3^{2-}$ ,  $C_2H_3O_2^-$ ,  $CN^-$ ; (4) "intermediate," characterized by medium values of all energy characteristics; examples are  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Fe^{2+}$ ,  $Ag^+$ ,  $Cu^+$ ,  $Cd^{2+}$ , and the addends  $NH_3$ ,  $C_2H_5(NH_3)_2$ ,  $NO_2^-$ ,  $HCO_3^-$ . Phenomena of group selectivity in complex formation and differences of stability of complex ions in soln. can be interpreted from this point of view.

N. Thon



YATSIMIRSKIY, K. B.

CA

Formalopentammine salts of cobalt(III). V. K. II.  
Yatsimirskii. Zhur. Obshchei Khim. (J. Gen. Chem.)  
20, 1408-II(1950).—Two new complex salts of Co(III)  
were synthesized.  $[\text{Co}(\text{NH}_3)_5\text{HCO}_3]\text{I}$  (I), red crystals,  
was obtained with a 95% yield by 40-min. heating 5 g.  
of Co purpureochloride,  $[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2$ , with 100 ml.  
of a concd. soln. of  $\text{HCO}_3\text{K}$  contg. approx. an 8-fold  
excess of  $\text{HCO}_3\text{K}$ , subsequent mixing of the cooled red  
soln. with an equal vol. of satd. KI, and washing the ppt.  
with ice water, aq. alc., and finally 90% alc. With a  
satd. soln. of  $\text{NH}_4\text{NO}_3$  instead of KI, a red ppt. of  $[\text{Co}(\text{NH}_3)_5\text{HCO}_3](\text{NO}_3)$  (II) was obtained in a 90% yield.  
The heats of reaction with a 0.26 M soln. of  $\text{Na}_2\text{S}$  at 25°  
were detd., for I, to be -3110 cal., and for II, to be -4560  
cal./mole. The heats of soln. in  $\text{H}_2\text{O}$  were detd. to be 14780  
and 16380 cal./mole, resp. Hence, and with the use of  
the thermochem. data of Blechowsky and Rossini, the  
standard heats of formation  $\Delta H_f^\circ$  of the solid salts were  
calcd. to be I -261.2, II -334.3 kcal./mole, and for the  
ion  $[\text{Co}(\text{NH}_3)_5\text{HCO}_3]^{++}$  in aq. soln., -219.7 kcal./mole.  
For the gaseous ion  $[\text{Co}(\text{NH}_3)_5\text{HCO}_3]^{++}$ , the heat of  
formation was calcd. to be 194 kcal./mole with the aid of the  
Kapustinskii equation for the lattice energy, with the  
thermochem. radius of the ion assumed = 2.36 Å. Hence,  
the heat of the reaction  $\text{Co}^{+++}(\text{gas}) + 5\text{NH}_3(\text{gas}) +$   
 $\text{HCO}_3^-(\text{gas}) = [\text{Co}(\text{NH}_3)_5\text{HCO}_3]^{++}(\text{gas}) + \text{IV}$  is  $x -$   
357 kcal., where  $x$  = heat of formation of the gaseous  
 $\text{Co}^{+++}$ . Consequently, the thermal stability of the gaseous  
 $[\text{Co}(\text{NH}_3)_5\text{HCO}_3]^{++}$  is greater than the stability of  
all other acidopentammine Co(III) ions, with the excep-  
tion of  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{++}$ . The stability of these com-  
plex ions decreases in the order  $\text{NO}_2^- > \text{HCO}_3^- > \text{CNS}^- >$   
 $\text{I}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^-$ . N. Thon



YATSIMIRSKIY, K. B.

Chem

Thermochemistry of complex compounds with ethylenediamine. K. B. Yatsimirskii and A. A. Astasheva. Chem. Tech. Inst., Lvov. Zhur. Obshchei Khim. (J. Gen. Chem.) 20, 2139-43 (1949).—Calorimetric measurements at 25° gave for the heats of the reaction of the complex salts with 1 N HCl the following values (en =  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ):  $[\text{Cd en}] \text{Cl}$  46.43;  $[\text{Cd en}] \text{Br}$  39.2;  $[\text{Ni en}] \text{Cl} \cdot 2\text{H}_2\text{O}$  39.00;  $[\text{Ni en}] \text{Br}$  37.04;  $[\text{Ni en}] \text{I}$  35.41 kcal./mole. From  $[\text{M en}] \text{X}_2$  (cryst.) + 6HCl aq.  $\rightarrow \text{M}^{++}$  aq. + 3 en  $\text{H}_2^{++}$  aq. + 6Cl<sup>-</sup> aq. + 2X<sup>-</sup> aq. +  $Q_1$ , and detns. of the heats of soln., the heats of formation of the complex salts in the standard state were calcd. to:  $[\text{Cd en}] \text{Cl}$  168.8,  $[\text{Cd en}] \text{Br}$  149.0,  $[\text{Ni en}] \text{Cl} \cdot 2\text{H}_2\text{O}$  163.1,  $[\text{Ni en}] \text{Br} \cdot 2\text{H}_2\text{O}$  148.0,  $[\text{Ni en}] \text{I} \cdot 2\text{H}_2\text{O}$  119.6,  $[\text{Ni en}] \text{Cl} \cdot 2\text{H}_2\text{O}$  309.7,  $[\text{Ni en}] \text{Br} \cdot 2\text{H}_2\text{O}$  200.4,  $[\text{Ni en}] \text{I} \cdot 2\text{H}_2\text{O}$  259.9,  $[\text{Cd en}]^{++}$  aq. 78.3,  $[\text{Ni en}]^{++}$  aq. 81.5 kcal./mole. The energy  $W$ , of binding of gaseous en by the gaseous metal ion  $\text{M}^{++}$ , to form the gaseous complex ion  $[\text{M en}]^{++}$ , is estd. from the lattice energy  $U$  of the cryst. complex salts,  $[\text{M en}] \text{X}_2$  (cryst.) =  $[\text{M en}]^{++}$  (gaseous) + 2X<sup>-</sup> (gaseous) -  $U$ , where  $U$  is calcd. by Kapustinskii's equation (C.A. 38, 5705<sup>2</sup>), with the thermochem. radii of all complex ions  $[\text{M en}]^{++}$  = 2.7 Å. This gives for  $W$ ,  $\text{Ni}^{++}$  383,  $\text{Zn}^{++}$  372,  $\text{Co}^{++}$  372,  $\text{Fe}^{++}$  342,  $\text{Cd}^{++}$  323 kcal./mole. The order of the heats of binding of 3 en by these ions is the same as that of the heats of binding of 6  $\text{NH}_3$ ; the latter are lower by 6-13 kcal. From the difference of the heats of formation of the anhyd. and the hydrated salts, the heats of hydration are calcd. to  $[\text{Ni en}] \text{Cl} \cdot 2\text{H}_2\text{O}$  10.3,  $[\text{Ni en}] \text{Br} \cdot 2\text{H}_2\text{O}$  5.9,  $[\text{Ni en}] \text{I} \cdot 2\text{H}_2\text{O}$  3.6. The abnormal increase of the heats of hydration from the iodide to the chloride can be explained by assuming hydration of the anion rather than the cation. N. T.

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CA

The solubility of complex salts. K. D. Vatsimirskii  
(Chem. Technol. Inst., Ivanovo). *J. Gen. Chem. U.S.S.R.*  
20: 2213-17 (1950) (Engl. translation). See *C.I.* 43,  
B. I. M.

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CM

Energetics of complex compounds. K. N. Yatsynskii  
(Chem. Technol. Inst., Ivanovo). *Izv. Vses. Khim.*  
(*Drugikh Vses. Akad. Inst. Obshch. i Org. Khim.*,  
Ibid. Nauk S.S.R. No. 23, 6-20 (1951)).—An extensive  
discussion of previous work (C.A. 42, 4888, 1948).  
M. Hosh

1951

**Thermochemistry of the trans influence.** K. H. Yates  
 univ. Chem. Technol. Inst. Doklady  
 Akad. Nauk S.S.S.R. 74, 307-10 (1980). With the heat  
 of formation of the hydrated  $\text{Co}^{++}$  ion assumed to be  
 $\Delta H_{\text{f}}^{\circ} = 22$  kcal. (from the free energy, with the entropy  
 $\Delta S_{\text{f}}^{\circ}$  of the ion in soln. taken equal to that of  $\text{Fe}^{++}$ ), the  
 following heats of formation of the complex ion in soln.  
 (from the hydrated central ion and addends) are calculated:  
 $[\text{Co}(\text{NH}_3)_6]^{++}$  (I) 4.9;  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{++}$  (II) 53.1;  
 $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{++}$  (III) 41.7;  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}]^{++}$  (IV)  
 $45.0$ ;  $1.6[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_2]^{++}$  (V) 53.1;  $1.2[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^{++}$  (VI) 32.0;  
 $1.2[\text{Co}(\text{NH}_3)_3\text{H}_2\text{O}]^{++}$  (VII) 30.2;  $1.6[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_3]^{++}$  (VIII) 43.0;  
 $1.2[\text{Co}(\text{NH}_3)_2\text{Cl}_4]^{++}$  (IX) 40.3;  $1.6[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{H}_2\text{O}]^{++}$  (X) 45.0;  
 $[\text{Co}(\text{NH}_3)(\text{NO}_2)_5]^{++}$  (XI) 47.0;  $[\text{Co}(\text{NH}_3)_6]^{++}$  (XII)  
 $28.1$  kcal. From these data, the heats of displacement of  
 $\text{NO}_2$  by  $\text{NH}_3$  are: V  $\rightarrow$  II, 0.0; VI  $\rightarrow$  III, -0.8; II  $\rightarrow$  I,  
 $-1.2$ ; X  $\rightarrow$  IV, -0.6; IX  $\rightarrow$  III, -7.6; XII  $\rightarrow$  VI,  
 $+18.9$ ; XI  $\rightarrow$  VI, +6.9; VI  $\rightarrow$  I, -2.0 kcal. Heats of  
 displacement of  $\text{NH}_3$  by  $\text{H}_2\text{O}$  are, V  $\rightarrow$  X, -7.5; II  $\rightarrow$  IX,  
 $-3.8$ ; III  $\rightarrow$  VII, -11.4; IX  $\rightarrow$  VII, -17.3 kcal. Heats  
 of displacement of  $\text{NH}_3$  by  $\text{Cl}^-$ : II  $\rightarrow$  IX, -3.4; I  $\rightarrow$  III,  
 $-3.8$ ; III  $\rightarrow$  VII, -0.7; III  $\rightarrow$  VIII, -11.5. Displace-  
 ment of  $\text{NH}_3$  by  $\text{H}_2\text{O}$ : II  $\rightarrow$  X, -7.5; I  $\rightarrow$  IV, -6.9.  
 Displacement of  $\text{H}_2\text{O}$  by  $\text{Cl}^-$ : X  $\rightarrow$  IX, +3.7; IV  $\rightarrow$  III,  
 $-3.3$  kcal. These figures illustrate the possibility of  
 thermochem. measurement of the trans influence. In the  
 case of  $\text{Co}^{++}$  complexes, the series is  $\text{NO}_2^- > \text{NH}_3$ ,  
 $\text{H}_2\text{O} > \text{Cl}^-$ . The susceptibility to trans influence de-  
 creases in that order, i.e. the heat effect accompanying the

displacement of  $\text{NO}_2^-$  is greatest when the trans position is  
 occupied by  $\text{NO}_2^-$ , somewhat smaller if it is occupied by  
 $\text{NH}_3$  or  $\text{H}_2\text{O}$ , and smallest with  $\text{Cl}^-$  in the trans position.  
 In the displacement of 2  $\text{NO}_2^-$ , the thermal effect is greatest  
 with XII, smaller with XI, and neg. with NH<sub>3</sub> in trans  
 position to  $\text{NO}_2^-$ . The same rules apply to displacement of  
 $\text{NH}_3$  and  $\text{H}_2\text{O}$  by  $\text{Cl}^-$ : the heat is greater with  $\text{NO}_2^-$  in  
 trans position to  $\text{NH}_3$  or  $\text{H}_2\text{O}$  than with  $\text{NH}_3$  or  $\text{Cl}^-$  in that  
 position. This order is reversed in the displacement of  $\text{Cl}^-$   
 $\text{NH}_3$  or  $\text{H}_2\text{O}$  by  $\text{NO}_2^-$ , and in the displacement of  $\text{Cl}^-$   
 by any of the addends considered. These facts can be  
 interpreted by assuming that, of the two d-, one s-, and  
 three p-bonds of the octahedron, the d-bonds are the most  
 stable, and that the different  
 addends have unequal tendency to occupy a d bond. This  
 tendency appears to decrease in the order  $\text{NO}_2^- > \text{NH}_3$ ,  
 $\text{H}_2\text{O} > \text{Cl}^-$ . For  $\text{NO}_2^-$ , the bond strength differs greatly,  
 depending on whether the  $\text{NO}_2^-$  group is bound by p- or  
 by d-bonds; this difference is less pronounced for  $\text{NH}_3$ ,  
 and  $\text{H}_2\text{O}$ , and seems to disappear completely for  $\text{Cl}^-$ .  
 This conclusion is borne out by the heats of formation  
 $\Delta H$  of geometric isomers. Cisocro-ions, with one  $\text{NO}_2^-$   
 group bound by a p-bond, the other by a d-bond, have a  
 lower  $\Delta H$  than flavo-ions, with both  $\text{NO}_2^-$  groups d-bonded.  
 In the case of praseo- and violco-salts, the trans isomer,  
 with the  $\text{Cl}^-$  ions bound by d- and p-bonds, has the higher  
 $\Delta H$ , probably as a result of the ionogenic nature of the  
 bond.

YATSIMIRSKIY, K. B.

Thermochemistry of complex compounds Moskva, Izd-vo Akademii nauk  
SSSR, 1951. (Mic 53-843 Collation of the original: 250 p.

Microfilm T-14



183T24

USSR/Chemistry - Analytical Reactions and Reagents Jul/Aug 51

"Classification of Analytical Reactions and Reagents on the Basis of the Energy Characteristics of Ions," K. B. Yatsimirskiy, Ivanovo Chem-Technol Inst

"Zhur Analit Khim" Vol VI, No 4, pp 211-217

"Covalent characteristic" of given ion, or tendency of ion to form covalent bond (calcd as difference between ion's ionization potential and its heat of hydration), electron charge, and ionic radius provide data for classification of ions for analyt

183T24

USSR/Chemistry - Analytical Reactions and Reagents (Contd) Jul/Aug 51

purposes. Gives tables of above values for many anions and gen rules for prediction of soly when particular anion and cation are present in soln.

183T24

YATSIMIRSKIY, K. B.

LC

Complex compounds with anions of aromatic sulfonic acids in the outer sphere. K. B. Yatsimirskiy, K. E. Pella, and V. V. Starostin (Chem.-Technol. Inst., Ivanovsk). Zhur. Obshchei Khim. (J. Gen. Chem.) 21, 480-90 (1951). Mixing 1% solns. of  $[Cr(NH_3)_6]Cl_3$  (I),  $[Cr(NH_3)_5(NO_2)]Cl_2$  (II), or  $[Cr(CON_2H_5)_3]Cl_3$  (III) usually gave ppt. of the corresponding complex salts.  $p$ -Me $_2$ C $_6$ H $_3$ SO $_3$ Na gave with I and III ppt. having compns. of the type  $[Cr(NH_3)_6](C_6H_4SO_3)_3$ . The soly. of the Cr salt is 0.0037 mole/l. at 20°. Na sulfonate does not give ppt. 2,4-CIMeC $_6$ H $_3$ SO $_3$ Na gives ppt. with I, II, and III;  $[Cr(NH_3)_6](C_{10}H_6ClSO_3)_3$ , yellow;  $[Cr(CON_2H_5)_3](C_{10}H_6ClSO_3)_3$ , yellow, soly. The 2-nitro analog gives ppt. with I, II, and III;  $[Cr(NH_3)_6](C_{10}H_6NSO_3)_3$ , green, 0.0087 mole/l. at 40°. The 2-chloro-5-nitro analog also soly. 0.0033 mole/l. at 20°.  $[Cr(NH_3)_6](C_{10}H_6ClNSO_3)_3$ , green. Na gives ppt. with I, II, and III;  $[Cr(NH_3)_6](C_{10}H_6ClNSO_3)_3$ , green.  $[Cr(CON_2H_5)_3](C_{10}H_6ClNSO_3)_3$ , green. Na gives ppt. with I, II, and III;  $[Cr(NH_3)_6](C_{10}H_6ClNSO_3)_3$ , green. 6-nitro-3-carbazolesulfonate gives ppt. even in rather dil. solns. with I, II, and III. Even less sol. are the salts of 6-nitro-3-carbazolesulfonic acid;  $[Cr(NH_3)_6](C_{10}H_6NSO_3)_3$ , yellow;  $[Cr(CON_2H_5)_3](C_{10}H_6NSO_3)_3$ , yellow; poorly sol. salts also form with derivs. of Cu, Zn, Ni, and Cd. Especially poorly sol. are salts of alizarinsulfonates; salts with I and II are especially mentioned but are not further characterized.

Generally, the soly. declines with increased size of the anion and with introduction of polar groups into it. Introduction of OH, NH $_2$ , or CO $_2$ H groups into the sulfonate radical sharply raises the soly. of the complex salts. Sepn. of some sulfonic acids by such means may be feasible. G. M. K.

10

Unsaturated cyclic hydrocarbons and their halogen derivatives. X. Transformation of unsaturated cyclic hydrocarbons.

184T33

YATSIMIRSKIY, K. B.

USSR/Chemistry - Analytical

Feb 51

"Problem of the Variation of Free Energy and Entropy in Reactions of Formation of Complexes," K. B. Yatsimirskiy, Chair of Analyt Chem, Chemicotech Inst, Ivanovo

"Zhur Fiz Khim" Vol XXV, No 2, pp 221-223

Advances hypothesis, based on entropy data for  $RO_2^-$  ions (i.e.,  $CO_3^{2-}$ ,  $MoO_4^{2-}$ ), that only thermochem ratios determine entropy of single-type complex ions (i.e., those having equal number of same groups combined to cen ion). Shows difference between heat effect and free energy to be const in single-type

184T33

USSR/Chemistry - Analytical (Contd)

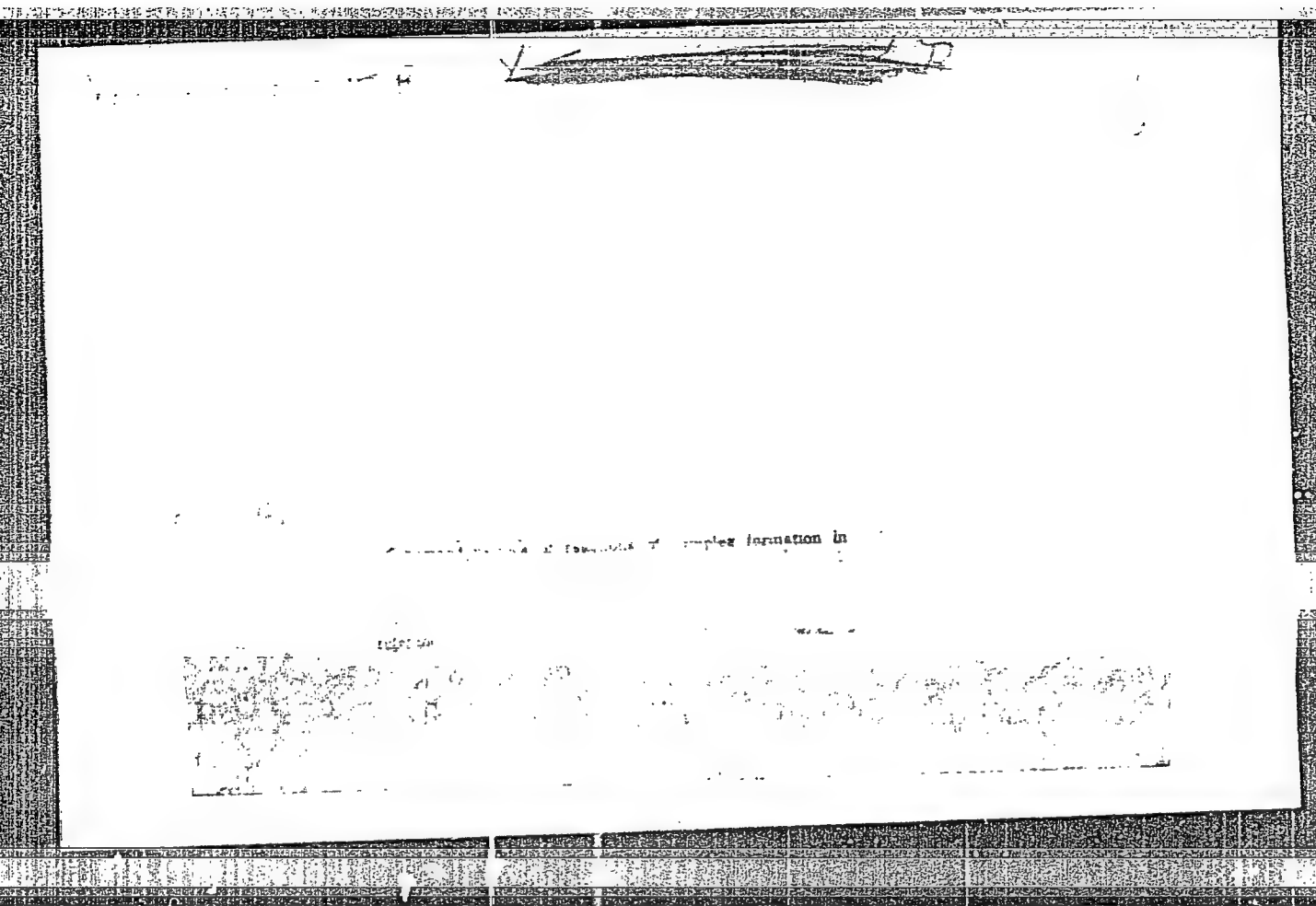
Feb 51

complex formation. Arranges anions and cations by decreasing stability, latter assumed to be detd by difference between ionization potential of cen atom and heat of hydration of ion formers.

184T33

CA

Stability constants of some complex compounds of lead.  
K. B. Yatsimirskii (Chem.-Tech. Inst., Ivanovo). *Zhur.*  
*Pri. Khim.*, 28, 478-9 (1951).—Earlier theoretical predictions  
(C.A. 43, 6114f) concerning the relative stability of com-  
plexes in soln. are verified by expts. leading to the detn. at  
25° of the stability const.  $K_1 = [Pb(S_2O_3)_2]^{-2}/[Pb^{2+}][S_2O_3^{2-}]^2$ ,  $K_2 = [Pb(S_2O_3)_3]^{-3}/[Pb^{2+}][S_2O_3^{2-}]^3$  and  $K = [Pb(CNS)_2]^{-2}/[Pb^{2+}][CNS^{-}]^2$ . The values  $K_1 = 1.35 \times 10^8$   
and  $K_2 = 2.23 \times 10^8$  are obtained by measuring the soly. of  
 $PbS_2O_3$  in aq. solns. of  $Na_2S_2O_3$ . The soly. product of  $PbS_2O_3$   
is also calcd.:  $3.90 \times 10^{-12}$ . The value  $K = 0.5$  is found  
by measuring the soly. of  $Pb(CNS)_2$  in aq. solns. of  $KCNS$ .  
The soly. product of  $Pb(CNS)_2$  is  $2.00 \times 10^{-12}$ . Finally, the  
stability const.  $K^* PbBr_2$  is estd. from the data of Burrage  
(C.I. 20, 342); it is approx.  $2 \times 10^3$ . These values of  $K_1$ ,  
 $K_2$ ,  $K$  and  $K^*$  confirm the theory. Michel Boudart



tential of the union element, i.e. from chlorate to iodine. In the search for analogous complexes with acidic cations other than Ag<sup>+</sup>, decans were made of the soly. of HgI<sub>2</sub> in aq. solutions of Hg(NO<sub>3</sub>)<sub>2</sub>; selected data are, for Hg(NO<sub>3</sub>)<sub>2</sub> · 0.1786, 0.7210, 1.2123, 1.4334, 1.8567 moles/(100 g. H<sub>2</sub>O), HgI<sub>2</sub> 14.5, 55.8, 110.3, 148.0, 209.3 millimoles/(100 g. H<sub>2</sub>O). The fast increase of the soly. indicates presence not only of HgI<sup>+</sup> but also of HgI<sub>2</sub><sup>·</sup>. From the soly. data, the equl consts. are [HgI<sup>+</sup>] = 1/[H<sub>2</sub>I] = 4.4 × 10<sup>-4</sup>, [HgI<sub>2</sub><sup>·</sup>] = 1/[H<sub>2</sub>I] = 2.1 × 10<sup>-3</sup>. Further complexes of this type are double salts variously described in the old literature, e.g., [AgS]<sup>+</sup>[Br]<sup>-</sup> which should be formulated [HgS]<sub>2</sub>X<sub>2</sub>, [CuS]<sub>2</sub>X<sub>2</sub>, [HgS]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>, [PbS]<sub>2</sub>X<sub>2</sub>, [AgS]<sub>2</sub>NO<sub>3</sub>, [HgS]<sub>2</sub>Cl<sub>2</sub>, [HgS]<sub>2</sub>Br; there are also more highly complex ions, such as [Hg<sub>2</sub>S]<sub>2</sub>X<sub>2</sub>. Examples of complexes with a d<sup>10</sup>-group element as central atom are the complexes described by Poleck and Thimmel (Ber. 10, 2435 (1881)), [Ag<sub>2</sub>I](NO<sub>3</sub>)<sub>4</sub>, [Ag<sub>2</sub>Se](NO<sub>3</sub>)<sub>4</sub>, and [Ag<sub>2</sub>Sb](NO<sub>3</sub>)<sub>4</sub>.

CA

The periodic law of D. I. Mendeleev and the stability of complex compounds. A. A. Grinberg and K. B. Yatsimskiy. *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1952, 211-17. —The tendency to complex formation is characterized quantitatively by the energies of formation of the gaseous complex ions, and by the instability const.  $K$  of the complex; the latter magnitude actually expresses the difference of the stability of the complex ion and of the corresponding aquo ion. From a thermochem. cycle involving the formation of a complex ion  $[MA_n]^{+n}$  from  $M^{+n} + nA$ , the heat is  $\Delta H = (W_1 - W_2) + (L_1 - L_2) + n(\lambda_1 - \lambda_2)$ , where  $W_1$  and  $W_2$  are the energies of soln. of  $M^{+n}$  and of  $A$ , resp., in the gaseous  $M^{+n}$ ,  $L_1$  and  $L_2$  are the heats of hydration of  $[MA_n]^{+n}$  and  $[M(H_2O)_n]^{+n}$ , resp., and  $\lambda_1$  and  $\lambda_2$  the heat of evapn. of  $H_2O$  and of hydration of  $A$ , resp. The latter term being const.,  $\Delta H = (W_1 - W_2) + C$  (const.), and  $RT \ln K = (W_1 - W_2) + C'$  (const.). This gives the relation between the 2 characteristics of the tendency to complex formation. This relation is verified by data for  $[Mg(NH_3)_6]^{++}$ ,  $[Co(NH_3)_6]^{++}$ ,  $[Ni(NH_3)_6]^{++}$ ,  $[Co en]^{++}$ ,  $[Ni en]^{++}$ , and  $[Zn en]^{++}$ . In application to ions with an inert-gas structure of the outer electron shell, but different charge and radius, this leads to the conclusion

that the stability of complexes increases from left to right in the period and decreases from top to bottom in the groups of the periodic system. For ions with 18-electron shells, the complex stability ought to decrease with increasing at. no. in the groups if the bond is predominantly ionic; with predominantly covalent bonding, elements of the 5th period should form particularly stable complexes. As a result of the 2 antagonistic factors, the heat of formation of gaseous complex ions within a subgroup may pass through a min.; examples are, for complex ions  $[M(NH_3)_6]^{+n}$ ,  $M = Cu$  131,  $Ag$  101,  $Au$  140 kcal./mole, and for ions  $[M(NH_3)_6]^{+n}$ ,  $M = Zn$  301,  $Cd$  311,  $Hg$  378 kcal./mole. The same is found for the free-energy change  $\Delta F = RT \ln K$  of formation of complex ions in aq. soln. The more pronounced the covalent character of the bond, the more marked is the increase of the stability ( $\Delta F$ ) of the complex ions from top to bottom; this is illustrated by comparison of  $\Delta F$  for complex chlorides, bromides, and iodides, the latter showing the most marked change of  $\Delta F$  from  $Cu$  to  $Au$  or from  $Zn$  to  $Hg$ , and the chlorides the least marked. In series of complex ions formed by central ions with the same charge, but with different outer-electron shell structures, the complex sta-

over



YATSIMIRSKIY, K.B.; ASTASHEVA, A.A.

Slightly soluble complex compounds of thiourea and their use in analysis.  
J. Anal. Chem. U.S.S.R. 7, 45-9 '52 [Engl. translation].  
(CA 47 no.19:9849 '53)

YATSIMIRSKIY, K.B.

Chemical Abst.  
Vol. 48 No. 8  
Apr. 25, 1954  
Analytical Chemistry

Thermodynamic criteria for the applicability of chemical  
reactions to volumetric analysis. K. B. Yatsimirskiy  
(Ivanovo Chem. Tech. Inst. I. J. Anal. Chem. 47, 1529,  
7, 23, 1952; Engl. translation) — See C.A. 47, 1529,  
H. L. H.

YATSIMIRSKIY, K. B., SHUTOV, A. A.

Mercury Compounds

Instability constants of complex mercury-iodide compounds. Zhur. fiz. khim. 16 no. 6, 1952

Monthly List of Russian Accessions. Library of Congress. November, 1952, Unclassified.

YATSIMIRSKIY, K.B.

3

Chemical Abst.  
Vol. 48 No. 9  
May 10, 1954  
Inorganic Chemistry

Some ternary complexes of copper and silver. K. B. Yatsimirskii and V. E. Panova (Vyssoye, Inst. Chem. Technol.). *J. Gen. Chem. U.S.S.R.* 22, 1325-33 (1952) (Engl. translation); *Zhur. Obshchei Khim.* 22, 1284-9 (1952).—When halides of Cu (I) and Ag dissolve in solus. of  $S_2O_3^{2-}$ , mixed complexes of the type  $[MeXS_2O_3]^{--}$  are formed. The solubilities of CuI and CuCNS in thio-sulfate solus. were measured at various temps., and the stability consts. were calcd. for the resultant  $[Cu(S_2O_3)_2]^{--}$  and  $[Cu(CNS)(S_2O_3)]^{--}$  as  $3.1 \times 10^{-11}$  and  $1.3 \times 10^{-11}$ , resp. On the basis of literature data for the solubilities of Ag halides in thiocyanate and thiosulfate solus., the following stability consts. were calcd.:  $[Ag(CNS)_2]^{--}$ ,  $1.0 \pm 0.5 \times 10^{-11}$ ;  $[Ag(CNS)]^-$ ,  $7.1 \times 10^{-12}$ ;  $[AgClS_2O_3]^{--}$ ,  $0.7 \times 10^{-10}$ ;  $[AgBrS_2O_3]^{--}$ ,  $4.1 \times 10^{-11}$ ;  $[AgIS_2O_3]^{--}$ ,  $2.7 \times 10^{-12}$ .

Bernard Rubin

9-2-54  
JRP

YATSMIRSKIY, K.B.

Chemical Abst.  
Vol. 48 No. 9  
May 10, 1954  
General and Physical Chemistry

The absolute contraction coefficient and the periodic law  
I. I. Zaslavskii and K. B. Yatsmirskii. *J. Gen. Chem.*  
(U.S.S.R.) 24, 1783-6 (1962) (Engl. translation).—See C.A.  
47, 1998c. H. L. H.

(2) Chem

9-2-54  
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YATSIMIRSKIY, K. B.

Chemical Abst.  
Vol. 48 No. 9  
May 10, 1954  
General and Physical Chemistry

② *Chem.*  
Thermochemistry of nickel-ammonia complexes in  
aqueous solution. V. K. B. Yatsimirskii and L. M. Grafova.  
*J. Gen. Chem. (U.S.S.R.)* 22, 1705-9 (1952) (Engl. transla-  
tion).—See *C.A.* 47, 2030c.  
H. L. H.

YATSIMIRSKIY, K. B.

Compounds, Complex

"Thermochemistry of complex compounds."  
Reviewed by O. Ye. Zvyagintsev. Zhur. prikl.  
khim, 25, No. 7, 1952.

Monthly List of Russian Accessions, Library of Congress, November 1952, UNCLASSIFIED.

YATSIMIRSKIY, K. B.

USSR/Chemistry - Cadmium and Lead  
Compounds

Feb 52

"Entropy Changes During Formation of Complex Halides  
in Aqueous Solutions," K. B. Yatsimirskiy, A. A.  
Astasheva, Ivanovo Chem-Technol Inst

"Zhur Fiz Khim" Vol XXVI, No 2, pp 239-243

Calcd entropy changes occurring during formation of  
some halide and cyanide complexes as well as std  
entropies for 11 complex ions and mols in aq soln  
(2 tables). Detd heats of mixing of  $Cd(NO_3)_2$  and  
 $Pb(NO_3)_2$  solns with KI solns. On the basis of exptl  
data, calcd heat effects of formation of ions

211749

$CdI_2$ ,  $PbI_2$ ,  $CdI_3$  in aq soln as well as contin-  
gent entropy changes. Showed that published re-  
sults on heats of formation of  $CdCl_2$  and  $PbI_2$  are  
in need of correction.

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*Organic Chemistry*

CA

Constants of instability of mercury-iodine complex compounds. (G. B. Yatsimirskii and A. A. Shutov (Chem. Technol. Inst., Ivanovo). *Zhur. Fiz. Khim.* 26, 842-7 (1952).) The soly.  $S$  of  $HgI_2$  in 0.028  $M$ , 0.090  $M$ , 0.268  $M$ , 0.593  $M$ , 1.844  $M$ , 1.058  $M$ , 1.345  $M$ , and 1.651  $M$   $Hg(NO_3)_2$  at 25° is 10, 85, 276, 443, 684, 926, 1290, and  $1638 \times 10^{-4}$  mole/l. Except the last two, these values can be represented by  $S = 0.0224 c^{1/2} + 0.0895 c^{3/2}$ , in which  $c$  is the concn. of  $Hg^{2+}$ , complete dissociation being assumed. The increase of  $S$  with  $c$  cannot be explained by the ionic strength  $I$  of the soln. as  $S$  increases with  $c$  also when  $I$  remains constant (in the soln. of  $Mg(NO_3)_2$  and  $Hg(NO_3)_2$  at  $I = 6$ ). As  $S$  contains terms in  $c^{1/2}$  and  $c^{3/2}$ , the increase of  $S$  is due to formation of  $[HgI]^+$  and  $[HgI_2]^0$  ions. From the above equation  $A_1K_1 = 0.0224$  and  $A_2K_2 = 0.0895$ ;  $A_2$  is the soly. product of  $HgI_2$  ( $\approx 10^{-12}$ ),  $K_1 = 7.06 \times 10^{-11}$  is the instability constant of  $[HgI]^+$ , and  $K_2 = 1.77 \times 10^{-11}$  is the instability constant of  $[HgI_2]^0$ . The soly. was determined in the usual manner and also by titrating  $Hg(NO_3)_2$  solns. with KI to opalescence. J. J. Bikerman.



YATSIMIRSKIY, K. B.

4

The calculation of the dissociation constants of stepwise complex formation from polarographic data. K. B. Yatsimirskiy (Chem. Technol. Inst., Ivanovo), *Sbornik State Obshchest. Nauch. S.S.S.R.* 1, 193-9 (1963).—  
The standard equations used for the calcn. of equil. consts. from polarographic data are derived on the assumption of a single equil. reaction,  $MX_{p-1}^{n-p+1} \rightleftharpoons M^{n+} + pX^{p-}$ . When stepwise complex formation occurs, it is necessary to add another equil.:  $MX_{p-1}^{n-p+1} \rightleftharpoons MX_{p-2}^{n-p+2} + X^{p-}$  (for notations cf. Stromberg, et al., *C.A.* 43, 5691e). This leads to relations that, upon differentiation and limitation to the case where the concn. of both complex ions is the same, become  $d\Delta E/d \log C_0 = A(p + 0.5)$  and  $\Delta E = A(\log C_0^{p+1} - \log K_{p+1} + \log 2)$ , where  $A = 0.059/n$ . The tangent for  $p = 1, 2$ , etc., is drawn to the  $\Delta E$  vs.  $\log c$  curve, and thus  $p$ ,  $\Delta E$ , and  $\log C_0$  are obtained. Dissocn. consts. of known complexes calcd. by this method agree with, or are of the same order of magnitude as, those calcd. by the older, simplified method. I. Benicowitz

1

Smol. J. K.

YATSIMIRSKIY, K.B.

**Stability of different degrees of oxidation of the elements.**  
K. B. Vysotskiĭ (Chem. Technol. Inst., Yanzovo)  
The author observed the stability of the oxidation states of the elements in the presence of air and water. The results are given in the form of a table.

... The system was ... The classification ... 44 ... 44 ... by the data of Syrovomskiy ... 44 ... the population actually exhibited higher degrees of ... of an element in the system ...

YATSIMIRSKII, K. B.

Chemical Abst.  
Vol. 48, No. 4  
Feb. 25, 1954  
Analytical Chemistry

chem 4  
(2)

The nature of the so-called "weighting effect." K. B. Yatsimirskii (Ivanov Chem. Technol. Inst.), *Zhur. Anal. Khim.* 8, 314-20 (1953).—The "weighting effect" first proposed by Feigl (*C.A.* 19, 1108) according to which an increase in the mol. wt. of a reagent increases the sensitivity of the latter toward a given reaction is not strictly true. The analysis outlined in *C.A.* 43, 1241i and 45, 3089e is applied here to org. reagents. It is shown that addn. of various groups into an analytical reagent causes a change in the free energy of its lattice. Replacement of H in a C—H group by some other group causes a change in the log of soly. ( $\Delta \log S$ ) by approx. the same value. For OH,  $\Delta \log S \sim 1.5$ , i.e. the soly. increases approx. 30 times. For other groups  $\Delta \log S$  is for  $\text{CH}_3$ ,  $-0.60$ ,  $\text{C}_2\text{H}_5$ ,  $-2.1$ ,  $\text{Cl}$   $-0.4$ ,  $\text{Br}$   $-0.5$ , and  $\text{I}$   $-1.0$ . The effect of added  $\text{CH}_3$  groups was studied on Li, Ca, and Ba fatty acid salts. For these salts  $-\Delta \log S/n$  was calcd. where  $n$  is the no. of  $\text{CH}_3$  groups. Each addn.  $\text{CH}_3$  caused the log  $S$  to decrease by an av. of 0.26. Addn. of aromatic rings caused a greater decrease in the soly. Addn. of hydrophobic groups causes a decrease in the soly. of the ppt. but at the same time reduces the soly. of the reagent which leads to a reduction of its sensitivity. M. Mosch

YATSIMIRSKIY, K.B.

Stability of complex compounds in aqueous solutions. Uspekhi Khim, 22,  
410-44 '53. (MLRA 6:4)  
(CA 47 no.19:9841 '53)

YATSIMIRSKIY, K.B

U S R

Redox potential and ionization potentials V. B. Yessimurakul

[illegible]

L. F. Casey

YATSIMIRSKIY, K.B.; GRANOVA, Z.M.

Thermochemistry of cuprammonium complexes in water solution. Zhur.ob.  
khim. 23 no.5:717-720 My '53. (MLRA 6:5)

1. Ivanovskiy khimiko-tehnologicheskii institut.  
(Thermochemistry) (Compounds, Complex)



YATSIMIRSKIY, K.B.

Chemical Abst.  
Vol. 48 No. 6  
Mar. 25, 1954  
Inorganic Chemistry

3.  
②  
Nickel-dimethylglyoxime complexes. K. B. Yatsimirskii and Z. M. Guralova. *Zhur. Obshchei Khim.* 23, 935-41 (1953).—The reaction between  $\text{NiSO}_4$  and dimethylglyoxime in ammoniacal soln. in the presence of atm.  $\text{O}_2$  yielded a colored (I) and a colorless (II) complex compd. The ratio of Ni:dimethylglyoxime in I was 1:3; in II, 1:1. The calcd. equil. const. checked well with the exptl., obtained by measuring the optical density of I at different concns. A. P. Kotloby

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11-5-54

YATSIMIRSKIY, K. B.

Instability constants of iodide-cadmium and iodide-lead complexes. K. B. Yatsimirskii and A. A. Shutov (Chem. Technol. Inst. Ivanovo). *Zhur. Fiz. Khim.* 27, 782-9 (1953); cf. *C.A.* 46, 11602d. — The calcd. instability const. of the complex ions  $(CdI)^{+++}$ ,  $(CdI)^{++}$ ,  $(PbI)^{+++}$ , and  $(PbI)^{++}$  at 25° were  $8.16 \times 10^{-4}$ ,  $8.41 \times 10^{-4}$ ,  $3.18 \times 10^{-4}$ , and  $6.05 \times 10^{-4}$ , resp., by measurement of the soly. ( $S$ ) of  $PbI_2$  in aq. solns. of  $Pb(NO_3)_2$  and  $Cd(NO_3)_2$  of various concns.  $S$  depended on the cation concns. according to the empirical equations  $S_1 = 0.037[Cd]^{1/2} + 0.0236[Cd]^{1/2}$  and  $S_2 = 0.0032[Pb]^{1/2} + 0.00075[Pb]^{1/2}$ . The calcd. relative activity coeffs. ( $\gamma$ ) of  $PbI_2$  in aq. solns. of  $Ca$ ,  $Mg$ , and  $Zn$  nitrates are tabulated for concns. of the latter from 0.2 to 2.4M; values of  $\gamma$  for  $PbI_2$  in satd. aq. soln. is arbitrarily equal to unity. The soly. product of  $PbI_2$ , calcd. from exptl. data by the method of Kapustinskii (*C.A.* 38, 2870<sup>1</sup>), is  $1.05 \times 10^{-4}$ .  
I. W. Lawchere, Jr.

[illegible]

YATSIMIRSKIY, K. B.

USSR/Chemistry - Cadmium, Palladium, Oct 53  
and Bismuth Compounds

"Thermochemistry of Complex Thiourea Compounds  
in Aqueous Solutions," K. B. Yatsimirskiy, A. A.  
Astasheva, Ivanovo Chem-Technol Inst

Zhur Fiz Khim, Vol 27, No 10, pp 1539-44.

Detd the heat of mixing of solns of the salts  
 $\text{AgNO}_3$ ,  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{CdBr}_2$ ,  $\text{CdI}_2$ ,  $\text{Pd}(\text{NO}_3)_2$ ,  
 $\text{Bi}(\text{NO}_3)_3$ , and  $\text{CuCl}_2$  with thiourea solns of dif-  
ferent concns. Detd the changes of enthalpy

272T12

and entropy in connection with the formation of  
complex ions from  $\text{Ag}^+$ ,  $\text{Cu}^+$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  with  
thiourea. Estimated the constant of instability K of  
 $[\text{Hg}(\text{thiourea})_4]^{2+}$  to be  $1.1 \times 10^{-33}$  on the basis  
of thermochemical data.

272T12

YATSIMIRSKIY, K.B.

USSR.

Use of dimethylphenylbenzylammonium as reagent for large anions. K. B. Yatsimirskiy and Z. I. Bergovoyshchenko. *Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 5(8) 90-3 (1954); cf. Emde, C.A. 3, 2470. —The  $\text{Me}_2\text{Ph}(\text{PhCH}_2)_2\text{N}^+\text{I}^-$  ion was added to solns. of different anions. I pptd.  $\text{Cr}_2\text{O}_7^{--}$ ,  $\text{S}_2\text{O}_8^{--}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ , and iodide. Sensitivity of these reactions was detd. The crystals were photographed. A 1M soln. of ICl was mixed with 0.5M solns. of salts of the anions. With  $\text{S}_2\text{O}_8^{--}$  white dendrites pptd. from concd. solns. (above 0.5%). Dil. solns. gave crystals. A 1M ICl soln. did not form a ppt. in solns. contg. <0.1%  $\text{S}_2\text{O}_8^{--}$  but when a ICl crystal was added to 1 drop of such dil.  $\text{S}_2\text{O}_8^{--}$  soln., crystals of  $\text{I}_2\text{S}_2\text{O}_8$  formed rapidly. Min. concn. was 1:2000, detectable min. 0.5  $\gamma$  (vol. of drop is 0.001 ml.). Soly. of  $\text{I}_2\text{S}_2\text{O}_8$  increased greatly by heating. The salt was recrystd. from hot  $\text{H}_2\text{O}$ , dried over  $\text{H}_2\text{SO}_4$ , and analyzed for S and N. With  $[\text{Fe}(\text{CN})_6]^{4-}$  yellow crystals,  $\text{I}_2\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  formed. Min. concn. was 1:2000, detectable min. 0.5  $\gamma$ . Compn. was confirmed by N and  $[\text{Fe}(\text{CN})_6]^{4-}$  detns. With  $\text{Cr}_2\text{O}_7^{--}$  yellow crystals with an unusual form pptd. from very dil. soln. Min. concn. was 1:2000, detectable min. 0.36  $\gamma$ . Analysis for  $\text{Cr}_2\text{O}_7^{--}$  confirmed the formula  $\text{I}_2\text{Cr}_2\text{O}_7$ . With  $[\text{Fe}(\text{CN})_6]^{3-}$ , ICl gave a ppt. only in the presence of acid. These fine greenish cubes are much less sol. in  $\text{H}_2\text{O}$  than the ferricyanide salt. Min. concn. was 1:17,000, detectable min. 0.058  $\gamma$ . Detn. of N and  $[\text{Fe}(\text{CN})_6]^{3-}$  confirmed the formula  $\text{I}_2\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ . From iodide solns. a crystal of ICl pptd. I iodide as confirmed by analysis. Min. concn. was 1:400, detectable min. 2.5  $\gamma$ . Burilla Mayerle

USSR/Chemistry

Card 1/1 Pub. 145 - 5/10

Author: APPROVED FOR RELEASE: 09/19/2001 CIA-RDP86-00513R001962310007-2"

Title : Energy characteristics and analytical classification of ions

Periodical : Zhur. anal. khim. 9/5, 282-292, Sep-Oct 1954

Abstract : The basic energy characteristics of ions, which determine mainly their behavior in a solution and the electro-affinity of the ion in an aqueous solution, are explained. Judging by the magnitude of electro-affinity all cations can be divided into three groups: ions with low electro-affinity forming water-soluble sulfides; ions with mean electro-affinity values forming sulfides soluble in acids but not in water, and ions with high electro-affinity forming non-soluble sulfides. All three groups belong to mono-, di- and tri-charge ions with an electro-affinity of 30, 70 and 190 kcal. Five USSR references (1950-1952). Tables.

Institution : .....

Submitted : November 26, 1953

YATSIMIRSKIY, K. B.

USSR/Chemistry

Card 1/1 Pub. 151 - IO/36

Authors : Yatsimirskiy, K. B., and Yasinskene, E. I.

Title : The kinetics of aquation of Cr urea complexes

Periodical : Zhur. ob. khim. 24/1, 55-61, Jan 1954

Abstract : The constants of the rate of reaction leading to the aquation of hexaurea-chromion in an aqueous solution were measured at 30, 40, 50 and 60° temperatures. The activation energy was computed. The rate of reaction of hexaurea-chromion activation was also investigated by an optical method and the results are listed. Seven references: 4-USA; 2-USSR and 1-German (1903-1952). Tables; graphs.

Institution : The Chemical-Technological Institute, Ivanovo

Submitted : September 14, 1953

*YATSIMIRSKIY, K. B.*

USSR/Chemistry

Card 1/1 : Pub. 151 - 5/42

Authors : Yatsimirekiy, K. B.

Title : Factors determining the stability of certain complex compound groups in aqueous solutions

Periodical : Zhur. ob. khim. 24/9, 1498-1507, Sep 1954

Abstract : The effect of increased central ion charge on the stability of complexes in aqueous solutions, especially in the case of addenda-anions with small radii or high charges, is explained. The stability of complexes with large addenda increases with the increase in radius of the central ion; the stability of complexes with small addenda and amino-acids decreases with increase in radius of the complex forming cation. The polarizing effect of isochoric ions was characterized by means of instability constants. Fifteen references: 4-USSR; 11-USA (1948-1953). Tables; graphs.

Institution : Chemical Technological Institute, Ivanov

Submitted : March 25, 1954

*YATSIMIRSKIY, K.B.*

USSR/ Chemistry - Physical chemistry

Card 1/1 Pub. 147 - 6/26

Authors : Yatsimirskiy, K. B., and Shutov, A. A.

Title : On the thermochemistry of certain iodide complexes

Periodical : Zhur. fiz. khim. 28/1, 30-35, Jan 1954

Abstract : The change in the heat content and entropy which occurs during the formation of complex ions  $[HgI]^+$ ,  $[CdI]^+$  and  $[PbI]^+$  was established from the experimental data regarding the heats of blending KI solutions with  $Hg(NO_3)_2$ ,  $Cd(NO_3)_2$  and  $Pb(NO_3)_2$  solutions. The specific heats of these solutions were established. The heats of formation of the iodide complexes were estimated on the basis of the heats of decomposition of solid complex  $[Ag_3I](NO_3)_2$  and  $[HgI]NO_3$  salts with water and  $Na_2S$  solutions. Six references 5-USSR and 1-French (1876-1953). Tables.

Institution : The Chemical Technological Institute, Ivanovo

Submitted : February 16, 1953



*YATSIMIRSKIY, K.B.*

GRINBERG, A.A. (Leningrad); BABAYEVA, A.V. (Moscow); YATSIMIRSKIY, K.B. (Ivanovo); GOREMYKIN, V.I. (Moscow); BOLIY, G.B. (Moscow); FIAT-KOV, Ya.A. (Kiyev); YAKSHIN, M.M. (Moscow); KEDROV, B.M. (Moscow); GEL'MAN, A.D. (Moscow); FEDOROV, I.A. (Moscow); MAKSIMYUK, Ye.A. (Leningrad); VOL'EENSHTeyN, M.V. (Leningrad); ZHDANOV, G.S. (Moscow); PTITSYN, B.V. (Leningrad); ABLOV, A.V. (Kishinev); VOLSHTEYN, L.M. (Dnepropetrovsk); TROITSKAYA, A.D. (Kazan'); KLOCHKO, M.A. (Moscow); BABAYEVA, A.V.; TRONEV, V.G. (Moscow); RUBINSHTeyN, A.M. (Moscow); CHERNYAYEV, I.I.; GRINBERG, A.A.; TANANAYEV, I.V.

Explanation of the transeffect. Izv.Sekt.plat.i blag.met. no.28:  
56-126 '54. (MLBA 7:9)

(Compounds, Complex) (Platinum)

YATSIMIRSKIY, K. B.

USSR/ Chemistry Physical chemistry

Card : 1/1 Pub. 11/7 - 17/25

Authors : Yatsimirskiy, K. B., and Zolotarev, E. K.

Title : On the thermodynamics of oxalate complexes

Periodical : Zhur. fiz. khim. 28/7, 1292 - 1298, July 1954

Abstract : Experimental data on the thermodynamics of oxalate complexes. The heat of blending solutions of homologous salts, with potassium and ammonium oxalate solutions, was determined for the purpose of estimating the enthalpy changes of such complexes. The instability constants of complex ions:  $Mn$ ,  $Co$ ,  $Ni$ ,  $Cu$ ,  $Zn$   $(C_2O_4)_2^{2-}$  and  $Fe$   $(C_2O_4)_3^{3-}$ , were determined. Nineteen references: 8 USA; 7 USSR; 1 Italian and 3 German (1903 - 1952). Tables; graph.

Institution : Chemical-Technological Institute, Ivanov

Submitted : November 16, 1953

~~YATSKINSKY, K. B.~~

DATE: 10/10/1961

1. 10. A new method for the estimation of the

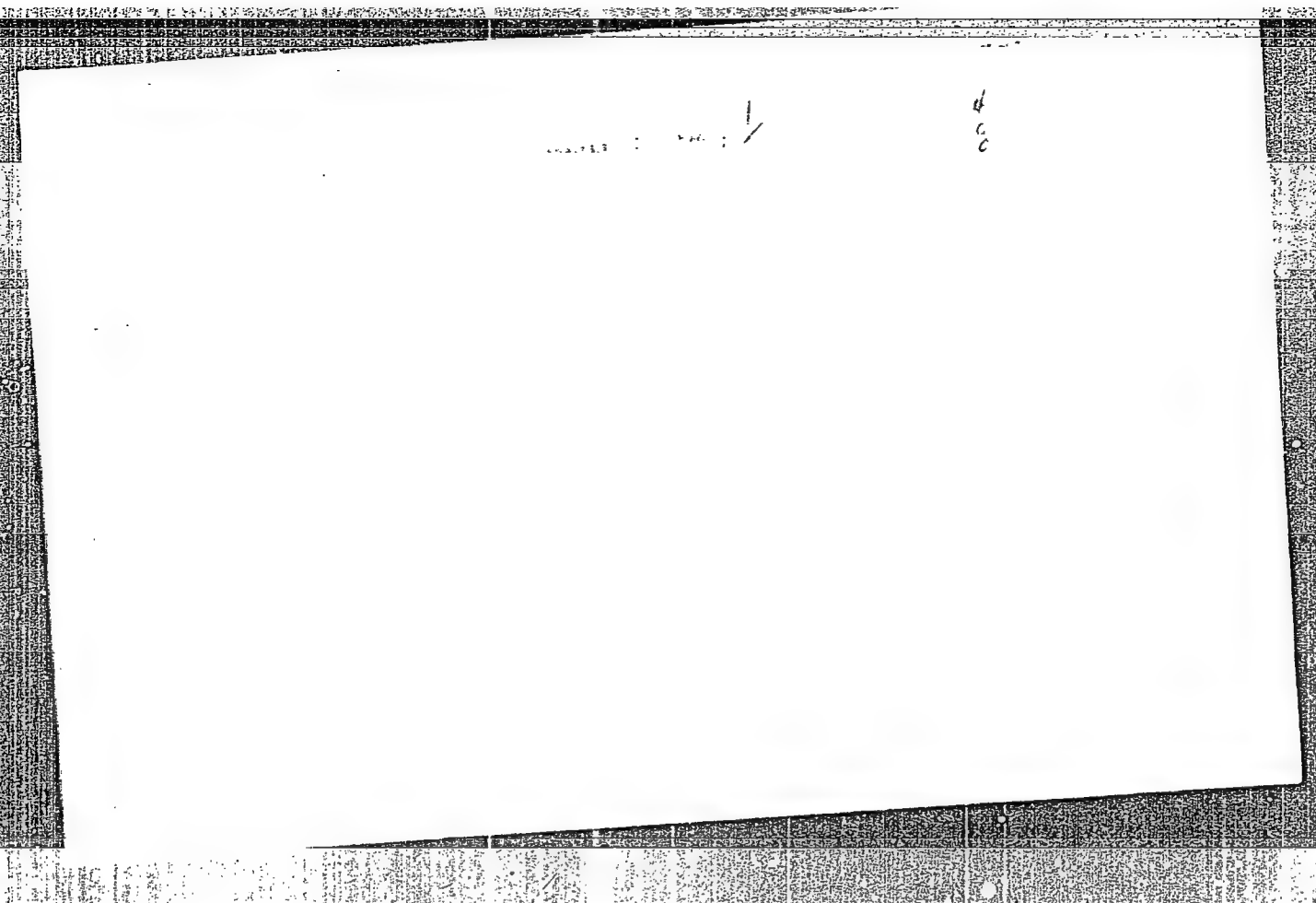
of the method for the estimation of the

YATSIMIRSKIY, K. B.

Quantitative characteristics which determine the suitability of complex compounds for volumetric analysis. Chik. B. Yatsimirski (Inst. Chem. Technol., Leningrad). Zhur. Anal. Khim. 10, 61-9 (1955); J. Anal. Chem. U.S.S.R. 10, 85-9 (1955) (Engl. translation).—In titration of complex-forming metals and in titration with such metals the max. degree of accuracy is detd. by the disocn. const. of the complex formed and by the initial concns. of the reactants. The accuracy of a titration is considered to be detd. by the ratio of the concn. of the given substance at the equivalence point to its initial concn. (cf. C.A. 47, 16205). The inverse logarithm of this ratio, designated by  $pT$ , is related to as the index of titration accuracy. For a reaction of the type  $M + A \rightleftharpoons MA$  a relation contg.  $pK$  (the inverse log of the disocn. const. of  $MA$ ) is derived, under the assumptions that the initial concns. of  $M$  and  $A$  are equal and that the changes in vol. upon titration are negligible. Where disocn. occurs in more than 1 step, the equation is somewhat more complex. The min. pH at which a titration with a certain degree of required accuracy can be carried out can be calcd. Fixing or masking accompanying elements into complexes is essential in certain cases of titration. The completeness of masking is detd. by the ratio of the equil. consts. of the masked and masking reactions and by the concns. of the reactants. A set of equations is derived which express the completeness of masking. In certain procedures of volumetric analysis the sought ion is first converted into a complex ion and then pptd. The applicability of this method depends primarily on the sol. product of the complex salt formed. Conditions for suitability of colored end-point indicators are derived. M. Hoegh.

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2



APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

Use of complexed is a synthetic chemical

YATSIMIRSKIY, K.B.

Application of complexons in analytical chemistry. II  
Feb 21, 1976 (1976)

YATSIMIRSKIY, K.B.

VASIL'YEV, V.P.; YATSIMIRSKIY, K.B.

On E.A.Uksho and A.I.Levin's article "Composition and properties of a complex electrolyte in a copper-pyrophosphate bath." Zhur. ob.khim.25 no.6:1233-1235 Je '55. (MIRA 8:12)

1. Ivanovskiy khimiko-tekhnologicheskii institut.  
(Electrolytes) (Uksho, E.A.) (Levin, A.I.)



YATSIMIRSKIY, K.V. (Ivanovo)

Thermodynamics of complex compounds of elements from the middle  
of the fourth period of Mendeleev's system. Uch.zap.Kaz.un. 115  
no.10:50-51 '55. (MLRA 10:5)

(Compounds, Complex)

YATSIMIRSKIY, K. B.

*YATSIMIRSKIY, K.B.*  
USSR/Physical Chemistry - Atom

B-3

Abs Jour: Ref Zhur-Khimiya, No 5, 1957, 14336

Author : Yatsimirskiy K. B.

Inst :

Title : Special characteristics of thirteen-electron ions

Orig Pub: Zh. neorgan. khimii, 1956, 1, No. 1, 96-99

Abstract: An examination is made of the relationship between the characteristics of bi- and trivalent ions of elements of the fourth period from Sc to Ga and the structure of the electron shells. It is shown that, in the series  $Ti^{2+}$ ,  $V^{2+}$ ,  $Cr^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ , and  $Sc^{3+}$ ,  $Ti^{3+}$ ,  $V^{3+}$ ,  $Cr^{3+}$ ,  $Mn^{3+}$ ,  $Fe^{3+}$ ,  $Co^{3+}$ ,  $Ni^{3+}$ ,  $Cu^{3+}$ ,  $Ga^{3+}$  (thirteen pelectron), the ions  $Mn^{2+}$ ,  $Fe^{3+}$  disturb the monotonous nature of the variation of certain characteristics: ionization potentials, oxidation potentials, ionic radii, heats of hydration, strength of compounds formed by these ions, vapor pressures of halide dissociation, crystalline structure of sulfides and

Card 1/2 Chemical Technol. Inst., Ivanovo.

USSR/Physical Chemistry - Atom

B-3

Abs Jour: Ref Zhur-Khimiya, No 5, 1957, 14336

Abstract: selenides of the type MX, rates of formation and decomposition of complex compounds. Disturbances of the monotony take place also in the case of  $Zn^{2+}$  and  $Ga^{3+}$ . All the disturbances are explained by the order in which the d-nuclei are filled by the electrons.

Card 2/2

*YATSIMIRSKIY K.B.*

USSR/Inorganic Chemistry - Complex Compounds, C

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 678

Author: Yatsimirskiy, K. B.

Institution: None

Title: Concerning Certain Functions Characteristic of Stepwise Complex Formation in Solutions

Original  
Periodical: Zh. neorgan. khimii, 1956, Vol 1, No 3, 412-421

Abstract: The basic functions which characterize stepwise complex formation in solutions are discussed: the "formation function"  $\bar{n}$ , the "degree of complex binding"  $\phi$  (giving the ratio of the total concentration of the metal to the concentration of free metal ions), the "fraction of the given complex"  $\alpha_m$  (giving the ratio of the concentration of a given complex ( $MA_m$ ) to the sum of the concentration of all complexes and the free metal ions). The relationships between  $\bar{n}$ ,  $\phi$ , and  $\alpha_m$  have been established, and the method for calculating any one of these functions from the others is indicated;  $\bar{n}$ ,  $\phi$ , and  $\alpha_m$  can be calculated from the

Card 1/2

USSR/Inorganic Chemistry - Complex Compounds, C

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 678

Abstract: experimental data obtained during the study of stepwise complex formation by the solubility method, the distribution coefficient, ion exchange, by the potentiometric method, by the polarographic method, etc. Formulas are given relating the functions under discussion to experimentally measured values. From a series of values of  $\bar{n}$ ,  $\phi$ , and  $\alpha_m$  it is possible to calculate the equilibrium constant for each step. Current methods for calculating the equilibrium constants are discussed and an improvement of a method previously proposed by the author is presented (Referat Zhur - Khimiya, 1954, 41064, 46234).

Card 2/2

YATSIMIRSKIY, K.B.

/ The kinetics and mechanism of the formation of urea 1

USSR/Inorganic Chemistry. Complex Compounds.

**YATSIMIRSKIY, K.B.**

Abs Jour : Referat. Zhurnal Khimiya, No 6, 1957, 18847

Author : K.B. Yatsimirskiy, I.I. Alekseyeva.

Inst : -

Title : Study of Oxalate and Phosphate Complexes of Molybdenum by the Kinetic Method

Orig Pub : Zh. Neorgan. Khimii, 1956, 1, No 5, 952-957

Abstract : The equilibrium in solutions of oxalate and phosphate complexes of Mo was studied on the basis of the measurement of the speed of the reaction of iodide oxidation by hydrogen peroxyde in an acid medium. This reaction is catalyzed by molybdic acid (I) (RZHKhim, 1956 78:55). A decrease of the concentration of I in consequence of the formation of complexes causes a corresponding decrease of the reaction speed. Oxalic and phosphoric acids were used in excessive amounts as complex producing reagents. The concentration of the  $H^+$  ions was 0.144 M. The kinetic study showed that I reacted with oxalic acid according to the equation:  $H_2MoO_4 + H_2C_2O_4 = [MoO_2C_2O_4]$

Card 1/2

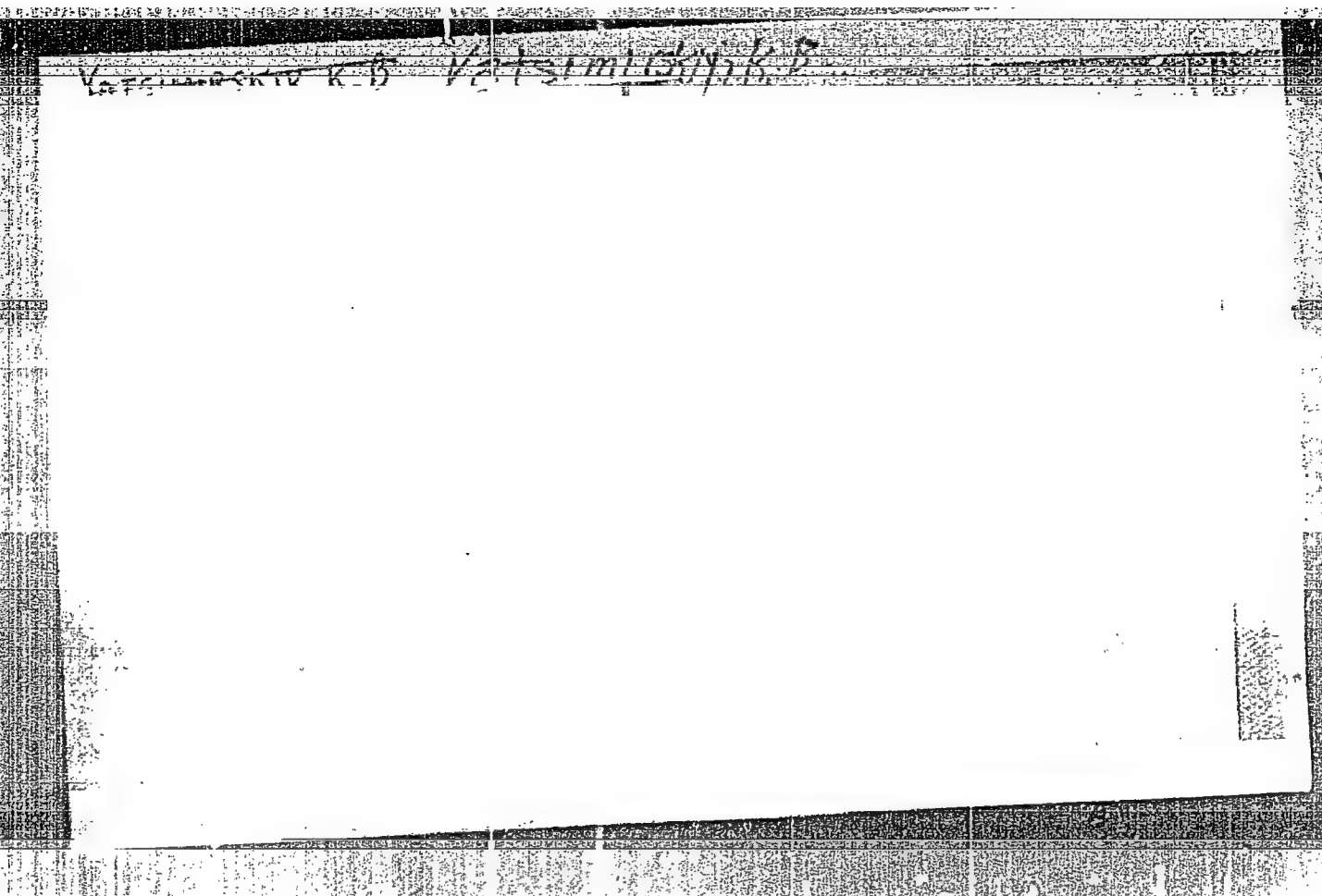
-26-



YATSIMIRSKIY, K.B.

"APPROVED FOR RELEASE: 09/19/2001

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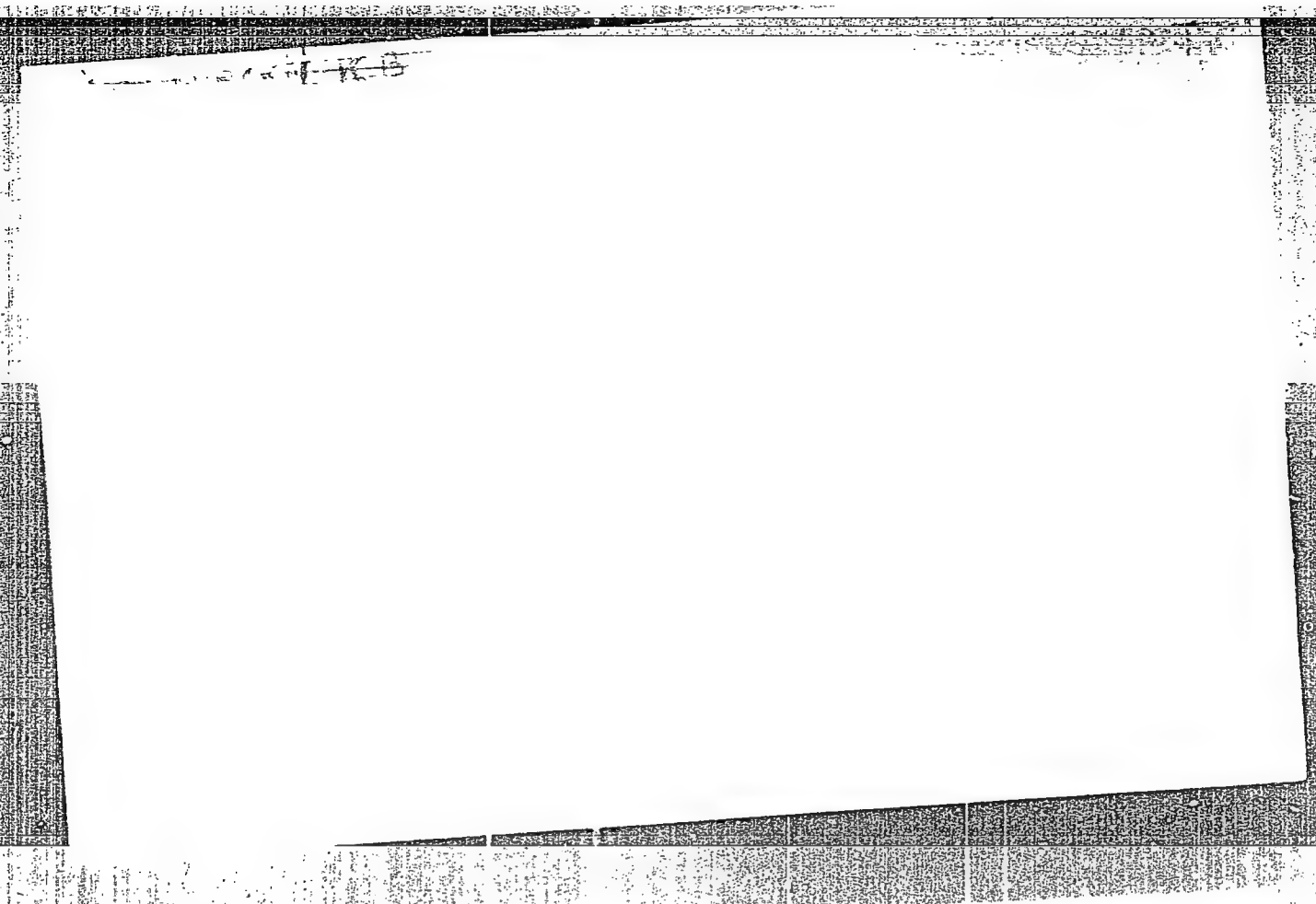
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YATSIMIRSKIY, K.B.

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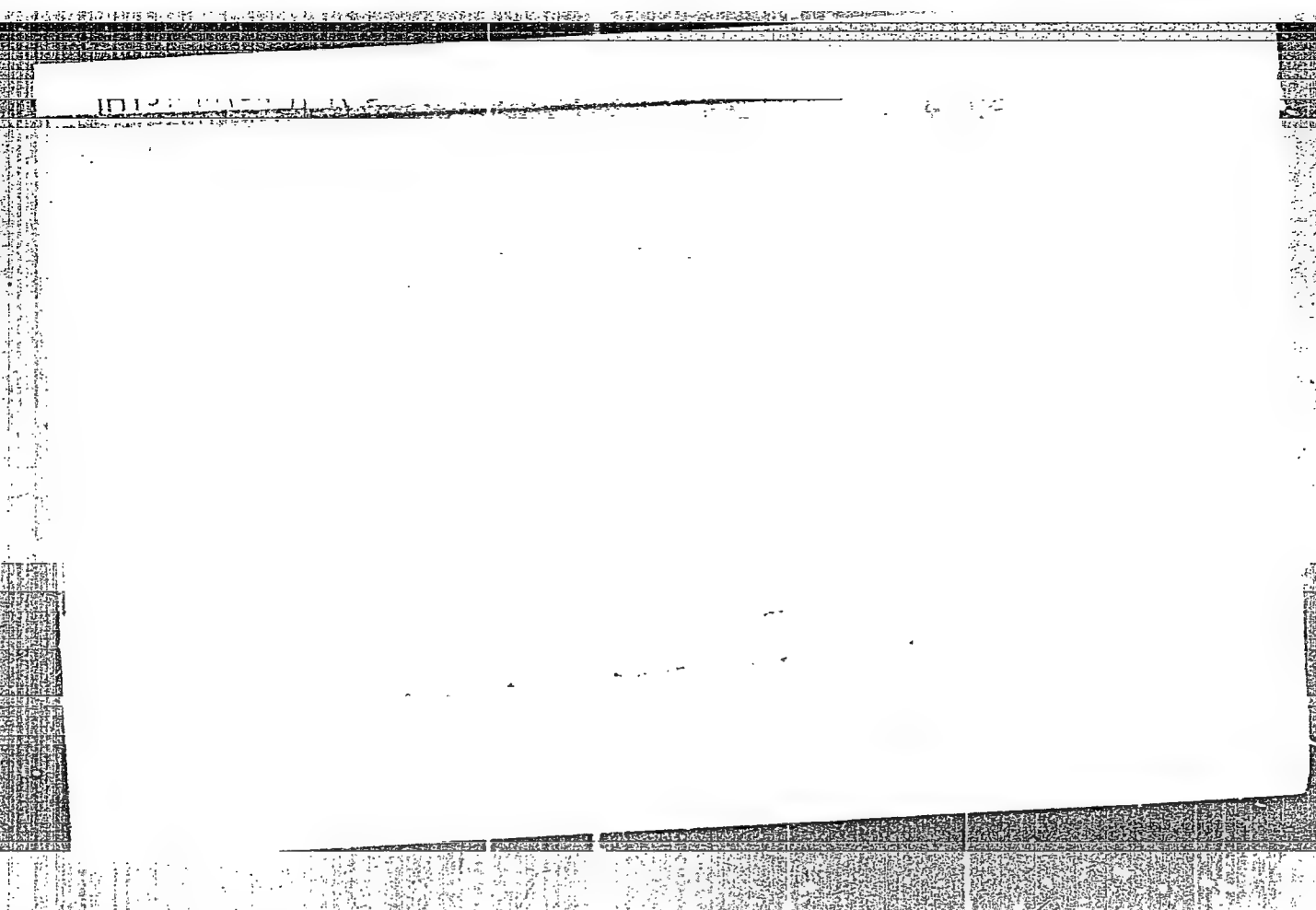
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11/00/6

APPROVED FOR RELEASE: 09/19/2001

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YATSIMIRSKIY, K B.

Kinetic methods of quantitative analysis. III. Deter-

made with 1.01 x 10<sup>-3</sup> mole of 0.103 g. per 10



Yatsimirskiy, K.B.

G-1

USSR/ Analytical Chemistry - General Questions

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11981

Author : Yatsimirskiy K.B., Astasheva A.A.  
Title : Use of Solutions of Thiourea in Volumetric Analysis (Thiocarbamidometry)

Orig Pub : Zh. analit. khimii, 1956, 11, No 4, 442-446

Abstract : To 10-25 ml 0.025-0.2 M solution of thiourea (I) is added an indicator (15-20 drops of saturated solution of diphenylcarbazide (II) in alcohol or 10 drops of an analogous solution of -nitroso- $\alpha$ -naphthol (III)), the mixture is diluted to 100-150 ml and titrated with a solution of  $Hg(NO_3)_2$ . On addition of II the solution acquires, at the transition point, a blue-violet coloration, while on addition of III it changes color from yellowish-green to yellowish-orange. Mean quadratic deviation is of 0.2-0.3% with II, and 0.1-0.2% with III. Back titration is also possible, although it is more appropriate, in the determination of Hg,

Card 1/2

G-1

USSR/ Analytical Chemistry - General Questions

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11981

to add a predetermined excess of I, and to titrate it thereafter with a solution of  $Hg(NO_3)_2$ . A pH value of 2 is optimal.  $Ag^+$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Mn^{2+}$ ,  $Mg^{2+}$ ,  $NH_4^+$ ,

$CH_3COO^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$  and  $PO_4^{3-}$  do not interfere. I is used

also in the determination of Cd. To 20 ml of Cd-salt under study (0.01-0.05 M) are added 20 ml 0.25 M solution of I, 30-40 ml of saturated solution of picric acid, and the volume is brought up to 100 ml. After 15-20 minutes it is filtered through a dry filter and an aliquot portion (20 ml) is titrated with 0.25-0.05 M solution of  $Hg(NO_3)_2$ , using II as indicator. Mean quadratic deviation 0.23%. Lowest limit of determination  $5 \cdot 10^{-4} M$ . Determination is interfered with by Hg, Bi, Ag, Cu, Tl and large amounts of Pb. A 1000-fold excess of Zn does not decrease the accuracy, but delays substantially separation of precipitate.

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APPROVED FOR RELEASE: 09/19/2001

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YATSIMIRSKIY, K. B.

USSR/Analytical Chemistry - General Questions, G-1

Abst Journal: Referat Zhur - Khimiya, No 19, 1956, 61780

Author: Yatsimirskiy, K. B., Gruin, I. P., Kashirina, F. D.

Institution: None

Title: Determination of the pH of Alkaline Solutions by Means of Light Filters

Original

Periodical: Zavod laboratoriya, 1956, 22, No 3, 271-273

Abstract: For determination of pH of alkaline solutions by means of a set of indicators and a photometer with light filters (Referat Zhur - Khimiya, 1955, 21380) the following indicators are suitable: tropeolin 000, eosin, 2,4-nitrophenyl-azo-1-naphthol-4,8-disulfonic acid Na salt, alizarine red and tropeolin O. The pH interval is 7.5-13.4. Error of the method ~0.1. At very high values of pH the presence in the solution of ions carrying a large charge interferes.

Card 1/1

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

VATSIKIRIV K.B

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

YATSIMIRSKIY, K. B.

USSR/Physical Chemistry - Crystals, B-5

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 195

Author: Kapustinskiy, A. F., and Yatsimirskiy, K. B.

Institution: None

Title: Lattice Energy of Salts Formed by Ions with 8-Electron Outer Shells

Original

Periodical: Zh. obshst. khimii, 1956, Vol 26, No 4, 941-948

Abstract: In the formula for the calculation of the energy of the crystal lattice  $U = 287.2 \frac{\sum n Z_K Z_A}{(r_K + r_A) \sqrt{1 - \rho / (r_K + r_A)}}$  (Kapustinskiy, Zh. obshst. khimii, 1943, Vol 13, 497) the value of the repulsion coefficient  $\rho$  depends on the sum of the ionic radii  $\rho = 0.345 - 0.00870 (r_K + r_A)^2$ . Using this empirical expression the following equation can be obtained:  $U = 287.2 \times \frac{\sum n Z_K Z_A}{(r_K + r_A) \sqrt{1 - 0.345 / (r_K + r_A) + 0.00870 \times (r_K + r_A)^2}}$ , which gives values of  $U$  which agree with experimental values within 2% for salts of the type  $MX$  and  $MX_2$ . The equation also gives satisfactory results for salts of the type  $MX_3$ . Considerable deviations are observed in the calculation of  $U$  for salts in

Card 1/2

USSR/Physical Chemistry - Crystals, B-5

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 195

Abstract: which the cations are highly polarized. The value of U has been calculated for the oxides, sulfides, and selenides of the elements in groups I and II of Mendeleyev's periodic system. The values of the electron affinity of the atoms O, Se, and S have also been calculated.

Card 2/2

YATSIMIRSKIY, K. B.

Category: USSR

C

Abs Jour: RZh--Kh, No 3, 1957, 7802

Author : Yatsimirskiy, K. B.

Inst : Not given

Title : On the Question of Step-By-Step Complex Formation

Orig Pub: Zh. Obshch. Khimii, 1956, Vol 26, No 7, 2083-2084

Abstract: A review article. See RZhKhim, 1956, 19015.

Card : 1/1

-23-

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

SECRETARY K B

APPROVED FOR RELEASE: 09/19/2001

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*YATSIMIRSKIY, K. B.*

USSR/Chemical - Physical chemistry

Card 1/1

Pub. 147 - 4/35

Authors : Yatsimirskiy, K. B., and Vasil'yev, V. P.

Title : Determination of instability constants of complexes by colorimetric measurement of the pH of the solution

Periodical : Zhur. fiz. khim. 30/1, 28-33, Jan 1956

Abstract : A new method was developed for colorimetric determination of pH in highly dilute sodium pyrophosphate solutions. The method was tested on several series solutions containing calcium nitrate and sodium pyrophosphate and was found to be perfectly suitable for such type of measurements. The instability constant of a calcium pyrophosphate complex was computed on the basis of results obtained by this new method. Five references: 3 USSR and 2 USA (1928-1954). Tables; graph.

Institution : Chemicotechnological Institute, Ivanovo

Submitted : March 14, 1955

YATSIMIRSKIY, K.B.

Category: USSR / Physical Chemistry  
Thermodynamics. Thermochemistry. Equilibrium. Physico-chemical analysis. Phase transitions.

B-8

Abs Jour: Referat Zhur-Khimiya, No 9, 1957, 29880.

Author : Yatsimirskiy K. B., Vasil'yev V. P.

Inst : not given

Title : Thermochemistry of Pyrophosphate Complexes in Solution

Orig Pub: Zh. fiz. khimii, 1956, 30, No 4, 901-911

Abstract: Determination of the heat of mixing values of solutions of nitrates of Ni, Cu, Zn and Pb with solutions of sodium pyrophosphate of different concentration, and also of the heat of dilution of the above-stated salts. The determinations were carried out in the previously described calorimeter (RZhKhim, 1955, 32011) which has been improved by the authors. From changes in heat of mixing value, with change in concentration of sodium pyrophosphate solution, the stepwise constant of instability of  $\text{Ni}(\text{P}_2\text{O}_7)^{4-}$  was calculated. Enthalpy change ( $\Delta H$ ) in the reaction  $\text{Ni}^{2+} \text{aq} + \text{P}_2\text{O}_7^{4-} \text{aq} = \text{NiP}_2\text{O}_7^{2-} \text{aq}$  (1) is  $4.21 \pm 0.04$  kcal.

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Card : 1/2

Category: USSR / Physical Chemistry.  
Thermodynamics. Thermochemistry. Equilibrium. Physico-  
chemical analysis. Phase transitions.

B-8

Abs Jour: Referat Zhur-Khimiya, No 9, 1957, 29880

Author : Yatsimirskiy K. B., Vasil'yev V. P.  
Inst : not given

In reactions of the type  $M^{+}aq + 2P.O_7^{2-}aq = M(P.O_7)_2^{2-}aq$  (2)  
the  $\Delta H$  for Ni, Cu, Zn and Pb is, respectively,  $2.00 \pm 0.02$ ;  
 $-0.67 \pm 0.07$ ;  $2.64 \pm 0.05$  and  $-1.01 \pm 0.11$ . Values of standard  
heat of formation have been calculated for the complex ions  $NiP.O_7$   
and  $M(P.O_7)_2^{2-}$  (M -- Ni, Cu, Zn and Pb). For reactions of type (2)  
change of isobaric thermodynamic potential and entropy have been  
calculated. Entropy change in these reactions satisfies the equa-  
tion:  $\Delta S = 0.1 L_{H_2O} + \text{const}$  (3), where  $L_{H_2O}$  is heat of hydration of  
 $M^{+}$  ion. Equation (3) is utilized to calculate the instability  
constant of  $Pb(P.O_7)_2^{2-}$  ion, together with the thermochemical  
data.

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Card : 2/2

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APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

DRAKIN, S. I. and YATSIMIRSKIY, K. B. (Ivanovo)

"The Entropy of Ion-Solvation,"

Report presented at Conference on the Effect of Solvents on the Properties of Electrolytes, Khar'kov, 14-16 Oct '57.

Zhurnal Fizicheskoy, Khimii, 1958, Vol 32, Nr 4, pp 960-962.

YATSIMIRSKIY, K. B.

"Determination of phosphate, sulfate, and molybdate."

report presented at The Use of Radioactive Isotopes in Analytical  
Chemistry, Conference in Moscow, 2-4 Dec 1957  
Vestnik Ak Nauk SSSR, 1958, No. 2, (author Rodin, S. S.)

YATSIMIRSKIY, K.B.

Observations on B.F. Ormont's article "Present state of the theory  
of complex compounds" (reports No.1 and 2). Zhur. neorg. khim. 2  
no.8:1975-1977 Ag '57. (MIRA 11:3)

(Complex compounds)  
(Ormont, B.F.)

566

AUTHORS:

Yatsimirskiy, K.B. and Tetyushkina, V.D.

TITLE:

Influence of Ionic Force on the Instability Constants of Halogen and Pseudo-Halogen Complex Compounds. (O Vliyanii Ionnoy Sily na Konstanty Nestoykosti Galogenidnykh i Psevdogalogenidnykh Kompleksnykh Soedineniy).

PERIODICAL:

"Zhurnal Neorganicheskoy Khimii" (Journal of Inorganic Chemistry, Vol.11, No.2, pp.320-329. (U.S.S.R.) -1957

ABSTRACT:

The range of applicability of empirical equations such as that of Davies (9) and the concepts of ionic force is still undecided. The research described is a contribution on this problem and involved the optical investigation of the thiocyanate complex of iron in the visible part of the spectrum. Relatively low concentrations of ferric nitrate (0.004974 mol/litre) and potassium thiocyanate (0.0004977 mol/litre) were used, enabling a wide range of ionic forces, from 0.25 to 3.5, to be covered. The bromide complex was also studied. Potassium, magnesium and aluminium nitrates were used to produce definite ionic forces.

Determinations were thus made of the instability constants and of the influence on complex-formation equilibria in the systems  $Fe^{3+}$  - CNS- electrolyte and  $Fe^{3+}$  - Br- electrolyte. It was shown that the ionic-force concept is valid up to forces of the order of 1.5 if the accuracy limit for the instability-constant indices of the complexes is taken as  $\pm 0.1$ ;

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